Effect of Heat Treatment on High Hardness Zirconia Sprayed Coating by Means of Gas Tunnel Type Plasma Spraying†

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Abstract

It can be possible to form high quality zirconia sprayed coating by means of gas tunnel plasma spraying. Moreover high hardness coating can be obtained at a short spraying distance. In this paper, the effect of heat treatment on the characteristic of this high hardness zirconia coating was investigated, and the influence on the Vickers hardness and structure of the coating was discussed.

KEY WORDS: (High Hardness Coating), (Zirconia Coating), (Heat Treatment), (Gas Tunnel Type Plasma Spraying), (Short Distance Spraying), (Vickers Hardness), (X-ray diffraction)

1. Introduction

It has been obtained high quality ceramic coatings with a gas tunnel type plasma spraying, as compared to conventional ceramic coatings[1,2]. The mechanism of the formation of such ceramic coatings has been investigated in the previous study. And the characteristics of those spraying have been clarified at various spraying conditions[3,4].

Now, the high function ceramic coatings[5] are applied to a lot of fields such as electronics and so on. In these circumstances, plasma spraying method is recently noticed for using the excelent characteristics of ceramics such as corossion resistance, thermal resistance, wear resistance and also its density[6].

As described in the previous papers, Vickers hardness of the ceramic coating formed by the gas tunnel type plasma spraying is increased with decreasing spraying distance[2]. Moreover a higher Vickers hardness can be obtained in the case of a shorter spraying distance ($L < L_p$), at each power input[7,8].

Here, the spraying distance L_p, where the characteristics of the Vickers hardness of the coating change dramatically, was about 40 mm when $P = 20$–30 kW, which was about 10 mm longer than the plasma jet length l_p, which shows that the effect of plasma energy on the coating surface was very large.

In this way, by a short distance spraying can be obtained very high hardness ceramic coating. For example, Vickers hardness of alumina coating was $H_V = 1500$ at $L = 30$ mm, when $P = 30$ kW[7]. According to the measurement of the distribution of the Vickers hardness, these high hardness alumina coatings had a hardness layer near the surface.

Observing the microstructure of alumina coating in this high hardness layer, it was found that the cell size was very fine compared with other parts of coating.

By the short distance spraying can be also obtained very high hardness zirconia coating, whose hardness was $H_V =$ 1200 at $L = 30$ mm when $P = 33$ kW[8]. In this case, the Vickers hardness of the sprayed coating became 20% or 30% higher than that of conventional plasma spraying, and that the high hardness zirconia coating had no macro cracks.

By the way, the color of coating surface changes by the spraying condition of gas tunnel type plasma spraying. For example, in spite that the color of the used zirconia powder is yellow, the coating color was gray and/or black at short spraying distance, in the case of the coating of 100-150 μm thickness. And at $L = 20$ mm, the surface was very dark color. This is because deoxidization of zirconia generated by the plasma energy from the former study on the zirconia coating.

In this paper, the effect on the characteristic of this high hardness zirconia coating by heat treatment was investigated, and the influence on the Vickers hardness of the zirconia coating was clarified and the structure of the zirconia coating was discussed from the results measured by using X-ray diffraction method.

2. Experimentals

The gas tunnel type plasma spraying apparatus used in this study is shown in **Fig. 1**. In this case the gas divertor

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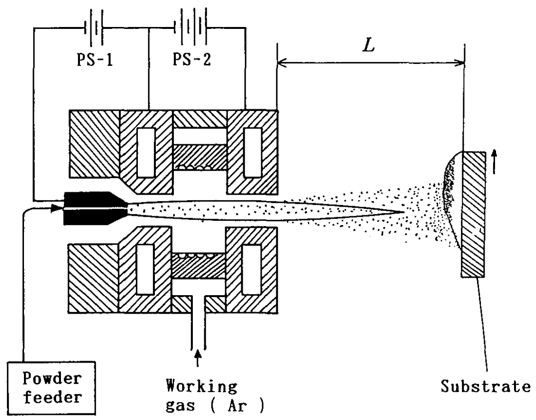

Fig. 1 Gas tunnel type plasma spraying apparatus, L: spraying distance, gas divertor nozzle diameter: $d = 15$ mm.

nozzle diameter was 15 mm. The experimental method to form high hardness ceramic coatings by means of the gas tunnnel type plasma spraying has been described in the previous papers[1-4]. In this study, the power input to the pilot plasma torch which was supplied by the power source PS-1 was zero after the generation of the gas tunnel plasma jet.

The experimental conditions for this plasma spraying of zirconia powder are shown in **Table 1**. The experiment was carried out mainly at short spraying distances ($L = 20$–50 mm). The traverse speed was rather low value of about 100 cm/min.

The chemical composition and the size of zirconia powder used in this study are shown in **Table 2**. This zirconia powder is commercially prepared type of K-90.

The Vickers hardness measurement of the sprayed coatings was carried out as follows. Here, we measured at the

Table 1 Spraying conditions, gas divertor nozzle diameter: $d = 15$ mm.

Power input	$P = 17 \sim 22$ kW
Working gas (Ar)	$Q = 220$ l/min
Powder carrier gas	10 l/min
Powder feed rate	$w = 18$ g/min
Traverse speed	$v = 96$ cm/min
Spraying distance	$L = 20 \sim 70$ mm

Table 2 Chemical composition and particle size of zirconia powder used.

Composition (wt%)					Size (μm)
ZrO_2	Y_2O_3	Al_2O_3	SiO_2	Fe_2O_3	
90.78	8.15	0.38	0.20	0.11	10～44

non-pore region in the cross section of the coating, in the condition that the load weight was 100 g, its load time was 25 s. The Vickers hardness was calculated as a mean value of 10 points measurement.

The cross sections of these zirconia coatings were observed by optical microscope and so on.

In order to investigate the structure of the zirconia coating, the X-ray diffraction method[9] was used. The X-ray source was Co, and the tube voltage was 30 kV and the tube current was 14 mA. This measurement was carried out on the surface of the coating.

To know the effect of the deoxidization, we formed the zirconia coating at $L = 30$ mm when $P = 20$ kW, whose color was gray. And for this coating, a heat treatment was carried out in air in a electric furnace at 800°C. The time of increasing temperature of this furnace was 1 hour and maintaining time of this temperature was also 1 hour. After heat treatment the specimens were naturally cooled in the furnace.

The change of the weight of the coating before and after heat treatment was measured to know the rate of the shortage of oxigen in the zirconia coating. And, the change of hardness distribution and X-ray diffraction patterns of the zirconia coating by means of the heat treatment were also measured.

3. Results and Discussion

3.1 Characteristicts of Vickers hardness

Figure 2 shows the relations between the spraying distance L and the Vickers hardness H_V on the cross sections of zirconia sprayed coatings which were formed by the gas tunnel type plasma spraying with gas divertor nozzle diameter of $d = 15$ mm.

As the spraying condition, Ar gas flow rate for gas tunnel type plasma spraying torch was $Q = 220$ l/min, the powder feed rate was $w = 17$ g/min, and the traverse speed of the substrate was $v = 96$ cm/min. And the power input to plasma torch was $P = 17$, 22 kW, respectively.

As described in the previous papers, Vickers hardness of the zirconia coating is increased with decreasing spraying distance[2]. Moreover a higher Vickers hardness can be obtained in the case of a shorter spraying distance ($L < L_p$), at each power input. In this case, the spraying distance was $L_p = 35$ mm when $P = 17$ kW, and $L_p = 44$ mm when $P = 22$ kW.

At the short spraying distance of $L = 30$ mm, when $P = 22$ kW, Vickers hardness of $H_V = 1050$ can be obtained. On the contrary, in the case of $d = 20$ mm, high power of $P = 33$ kW was needed for the formation of high hardness zirconia coating.

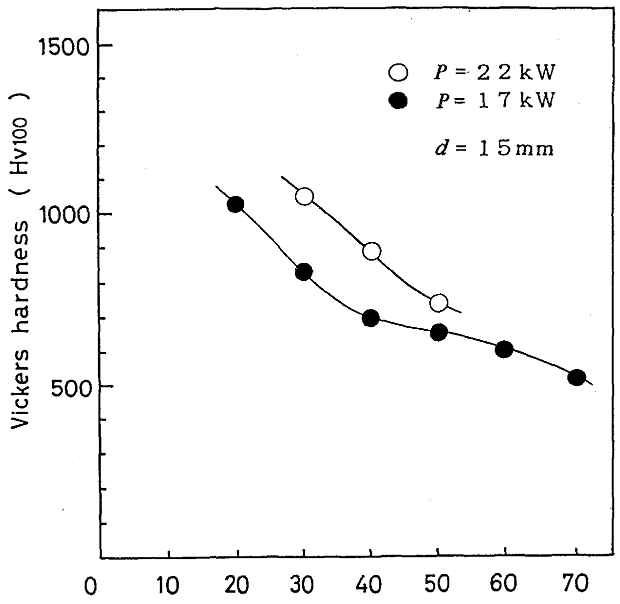

Fig. 2 Dependences of Vickers hardness of zirconia coating on spraying distance at $P=17$ kW and $P=22$ kW, gas divertor nozzle diameter: $d=15$ mm.

But when the power input was lower value of $P=17$ kW, the Vickers hardness of the spayed coating became a high value of $H_V=1000$, only at the shortest spraying distance of $L=20$ mm.

By the way, in the case of using $d=12$ mm of gas divertor nozzle, the Vickers hardness of the zirconia sprayed coating became 20% or 30% higher than that with $d=15$ mm dia. of gas divertor nozzle. And in these cases, the L_p was about 50 mm, when $P=24$ kW.

3.2 Distribution of Vickers hardness on the cross section of zirconia coating

Figure 3 shows the distribution of Vickers hardness on the cross section of zirconia coating in the gas tunnel type plasma spraying. The measurement was carried out at each distance from the coating surface in the thickness direction.

In this case, the power input to plasma jet was $P=20$ kW, Ar gas flow rate was $Q=220$ l/min and the spraying distance was $L=30$ mm. This coating was formed by two times traverse and the powder feed rate was small value of $w=17$ g/min in order to obtain the gray color coating. The thickness of this coating was about $t_c=120$ μm.

The distribution of the Vickers hardness became a parabolic curve as shown in this figure. It is found that the Vickers hardness near the coating surface (Y-axis) is higher than that near the substrate. The hardness is the highest at the distance from the coating surface of $l=40$ μm, whose

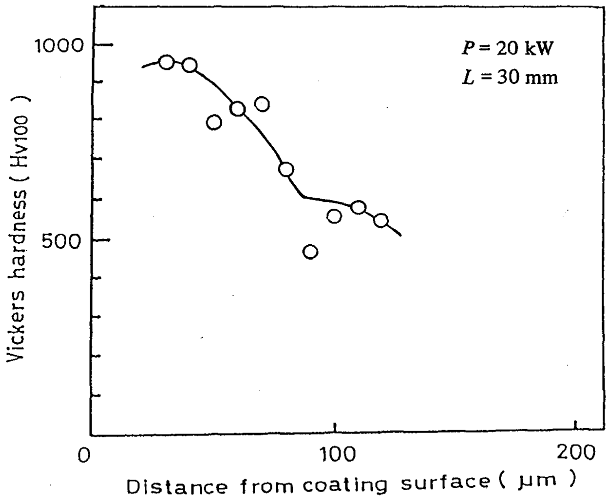

Fig. 3 Distribution of Vickers hardness on cross section of zirconia coating at spraying distance $L=30$ mm, when $P=20$ kW.

value is about $H_V=1000$.

Therefore in this high hardness zirconia coating, a high hardness layer which has the Vickers hardness of more than $H_V=900$ appears in the surface layer of the coating.

Figure 4 shows the photograph of the cross section of high hardness zirconia coating by an optical microscope, which is the same coating as that shown in Fig. 3. In this case, the power input was $P=20$ kW and the spraying distance was $L=30$ mm.

From observation of this sprayed coating, in the cross section the pore is a little, which is the same coating structure as described in the former paper. Moreover, the part near the coating surface the micro structure was very dense, which just corresponds to a high hardness layer of $H_V>900$, which was described in Fig. 3. However there exist some large pores because of the low power input.

3.3 Heat treatment of high hardness zirconia coating

The color of a high hardness zirconia coating of 100–150 μm thickness was gray under such spraying condition as the short spraying distance.

Therefore, the heat treatment was carried out for the zirconia coating formed at $L=30$ mm when $P=20$ kW, which is shown in Fig. 3 and Fig. 4. The thickness of this coating was $t_c=120$ μm and the color was gray. The condition of the heat treatment was at the temperature of 800°C, for 1 hour in air.

After heat treatment of this coating, the oxidization proceeded and the color of the coating was changed from gray to yellow which was the color of zirconia powder. From this result, it can be thought that by the oxidization due to the heat treatment in air, the color of zirconia

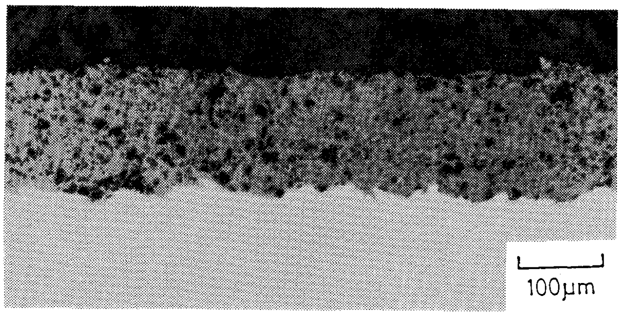

Fig. 4 Photograph of cross section of zirconia coating at $L=30$ mm, when $P=20$ kW.

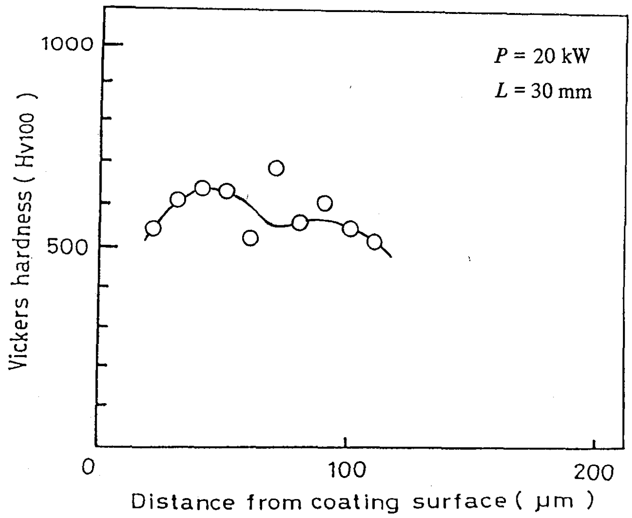

Fig. 5 Distribution of Vickers hardness on cross section of zirconia coating after heat treatment. (as sprayed at $L=$ 30 mm, when $P=20$ kW.)

coating was restored to original yellow from gray of the zirconia coating missing oxygen.

Then, from the change of the weight of the coating before and after heat treatmennt, the rate of the shortage of oxygen in the zirconia coating was calculated. As the result, in this case the rate of the shortage was 1.25 at%. This value is very small but the deoxidization in zirconia coating was confirmed. And the rate was increased to 3 at% in the case of zirconia coating with more dark gray.

3.4 Effect of heat treatment on high hardness zirconia coating

Figure 5 shows the distribution of Vickers hardness on the cross section of zirconia coating after the heat treatment.

In this case, as sprayed coating was the same coating as Fig. 3. The coating thickness was $t_c=120$ μm.

The distribution of Vickers hardness is also parabolic curve. The hardness near the substrate did not change as compared with as sprayed coating shown in Fig. 3. However, the Vickers hardness near the coating surface is much lower than that before heart treatment. The Vickers hardness of the coating is changed from $H_V=1000$ to $H_V=650$. Because the internal stress in the zirconia coating was relaxed by the heat treatment.

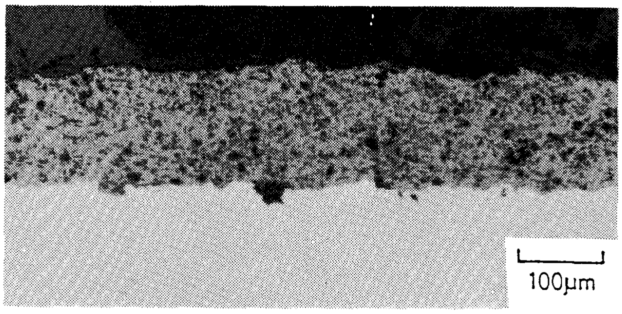

Fig. 6 Photograph of cross section of zirconia coating after heat treatment.

In this way, the zirconia coating after heat treatment has a flat distribution of Vickers hardness on the cross section in the thickness direction, whose value is about $H_V=650$, and a high hardness layer does not exist in this zirconia coating.

In the case of the coating after heat treatment, as mentioned above the Vickers hardness becomes lower and the hardness distribution becomes flatter.

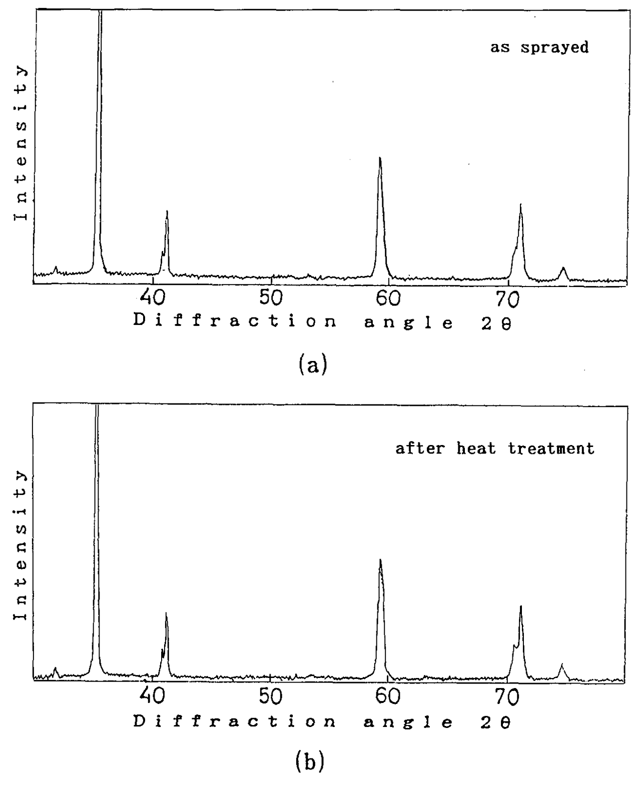

Fig. 7 X-ray diffraction patterns of the surface of zirconia coating at $L=30$ mm, when $P=30$ kW, (a) as sprayed, (b) after heat treatment.

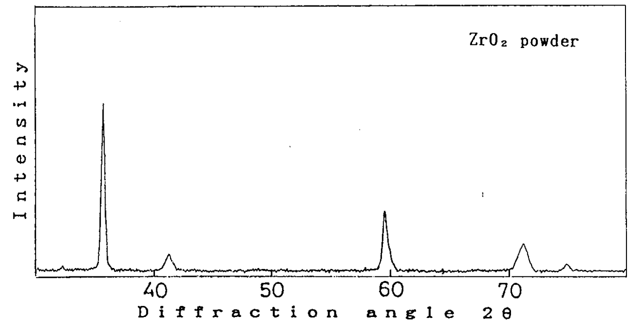

Fig. 8 X-ray diffraction pattern of zirconia powder.

Figure 6 shows the photograph of optical microscope of the cross section of zirconia coating after heat treatment, which is the same coating as that shown in Fig. 5.

From the observation of this sprayed coating, the pore was spreadened all over the cross section of the coating. But large difference does not observed as compared with as sprayed coating.

3.5 Structure of zirconia sprayed coating

The results obtained by means of the X-ray diffraction method of zirconia coating formed by the gas tunnel type plasma spraying are as follows.

Figure 7 shows the X-ray diffraction patterns of the surface of high hardness zirconia coating, which is the same coating as that shown in Fig. 3. In this case, the power input was $P=20$ kW and the spraying distance was $L=30$ mm. Here (a) is X-ray diffraction pattern of the coating as sprayed, and (b) is X-ray diffraction pattern of the coating after heat treatment.

From these results, the peaks near the degree of 40° and 70° appear splitting, which shows the existence of tetragonal ZrO_2. In tetragonal phase, two peaks obtained from (002) and (200) planes are 40.6° and 41.3° from ASTM card. And the crystal form of this zirconia coating which is tetragonal ZrO_2 did not change after the heat treatment. This was also confirmed by the Laser Raman Spectroscopy.

For the comparison, the X-ray diffraction pattern of zirconia powder used is shown in **Fig. 8**. The peaks near the diffraction angle of 40° and 70° are rather broader as compared with that of sprayed coating as shown in Fig. 7, and do not split, which is used to estimate the composition of the cubic phase[10]. This results show that by this plasma spraying the crystal form of the cubic ZrO_2 was transformed into a tetragonal phase.

On the other hand, after heat treatment of the zirconia coating, it appeared a little difference in the (002) and (200) regions of the diffraction pattern. **Figure 9** shows the diffraction patterns in the region of diffraction angle between 40° and 42°. which contains sub peak of 40.7° and main peak of 41.1°. Here (a) is that of as sprayed coating, and (b) is that of the coating after heat treatment.

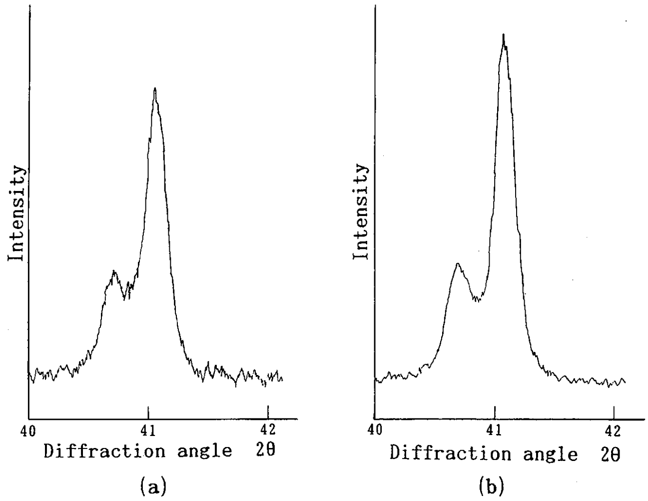

Fig. 9 The peaks of X-ray diffraction pattern of the surface of zirconia coating at $L=30$ mm, when $P=30$ kW, (a) as sprayed, (b) after heat treatment.

By heat treatment two peaks became clearer than of as sprayed coating. This was due to larger difference of diffraction angle of two peaks: the angular separation between the two tetragonal peaks was changed from $\Delta 2\theta=0.34°$ degrees to $\Delta 2\theta=0.39°$ degrees . This is thought that stabilization of zirconia which was tetragonal phase for as sprayed was advanced by the heat treatment.

4. Conclusion

Vickers hardness of zirconia coating is increased with decreasing spraying distance, and the characteristics of the Vickers hardness change dramatically at L_p, in the gas tunnel type plasma spraying with gas divertor nozzle diameter of $d=15$ mm. Thus a higher Vickers hardness of the coating can be obtained in the case of short distance spraying at each power input.

For example, Vickers hardness of zirconia coating was $H_V=1050$ at $L=30$ mm, when $P=20$ kW. The color of this coating was gray, but after heat treatment, this color changed to white yellow. This reason was thought that the zirconia was deoxidized by the heat of plasma.

According to the measurement of the distribution of the Vickers hardness, the high hardness coating had a hardness layer near the surface. The hardness of this high hardness layer became lower after the heat treatment.

Observing the microstructure of the zirconia coating in this high hardness layer, it was found that the structure was dense compared with other parts of coating. But the coating structure after heat treatment was almost the same structure of as sprayed coating.

From the results obtained by means of the X-ray diffraction method, it showed that by this plasma spraying the crystal form of the cubic ZrO_2 of powder was transformed into a tetragonal phase. And the crystal form of this zirconia coating which was tetragonal ZrO_2 was not change by the heat treatment.

By heat treatment the angular separation between the two tetragonal peaks from (002) and (200) planes became broader. This was thought that the crystal form of zirconia which was tetragonal phase for as sprayed was stabilized by the heat treatment.

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