Title	Effect of Thermal Process on High Hardness Zirconia Coating by Means of Gas Tunnel Type Plasma Spraying(Physics, Process, Instruments & Measurements)
Author(s)	Kobayashi, Akira; Yamahuji, Katsuhiro; Kitamura, Tahei
Citation	Transactions of JWRI. 1991, 20(2), p. 165-171
Version Type	VoR
URL	https://doi.org/10.18910/7914
rights	
Note	

Effect of Thermal Process on High Hardness Zirconia Coating by Means of Gas Tunnel Type Plasma Spraying

Akira KOBAYASHI*, Katsuhiro YAMAHUJI, Tahei KITAMURA*****

Abstract

By means of gas tunnel type plasma spraying, a high hardness zirconia coating could be obtained at a short spraying distance. For example, Vickers hardness of zirconia coating was $H_V = 1050$ at $L = 30$ mm, when $P = 20$ kW. This high hardness coating had a high hardness layer near the surface. The hardness of this high hardness layer became lower after heat treatment. The crystal form of the cubic ZrO_2 of powder was transformed into a tetragonal phase through this plasma spraying. After heat treatment, the angular separation between the two tetragonal peaks was broader and clearer. In this paper, the effect of thermal process (include heat treatment) on the characteristic of such a high hardness zirconia coating was investigated, and the influences on the Vickers hardness and structure of the coating were discussed.

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

1. Introduction

Characteristics of Vickers hardness of ceramic sprayed coatings which were formed by the gas tunnel type plasma spraying was investigated in the previous studies[1,2,3]. And the relations between the spraying distance L and the Vickers hardness H_V on the cross sections of ceramic (zirconia) sprayed coatings were clarified[4].

In zirconia coating by means of the gas tunnel type plasma spraying, the Vickers hardness of the cross section was increased with decreasing spraying distance[5], and higher Vickers hardness could be obtained in the case of a shorter spraying distance ($L < L_p$)[6]. In this case, the critical spraying distance L_p at which the characteristic of the Vickers hardness changed was about $L_p = 40$ mm, when $P = 20$ kW.

At a short spraying distance of $L = 30$ mm, when $P = 20$ kW, the Vickers hardness of zirconia coating was about $H_V = 1050$ in the case of gas divertor nozzle diameter of $d = 15$ mm[7].

According to the distribution of the Vickers hardness on the cross section of this zirconia coating, it was found that a high hardness layer of $H_V > 900$ appeared near the surface. In this high hardness layer the pore was a little and the microstructure was very dense.

The hardness of this high hardness layer became lower after heat treatment, and the Vickers hardness distribution becomes flatter. However, it is found that clear change did not appear before and after heat treatment in the microstructure of the zirconia coating in this high hardness layer.

By the way, the color of this coating was gray under the spraying condition: $P = 20$kW, $L = 30$ mm, but after heat treatment, this color changed into white yellow. This reason is thought that the zirconia coating as sprayed was deoxidized by the heat of plasma to miss oxygen.

Through heat treatment of this coating, the oxidization proceeded and the color of the coating was changed from gray to yellow which was color of zirconia powder. At this time, the rate of the shortage of oxygen was 1.25 at%, and the deoxidization in zirconia coating was confirmed.

The crystal form of the cubic ZrO_2 of powder was transformed into a tetragonal phase[8,9] by plasma spraying. And after heat treatment, the angular separation between the two tetragonal peaks from (002) and (200) planes was broader and became clearer than that of as sprayed coating. But the crystal form of this zirconia coating which is tetragonal ZrO_2 did not change after heat treatment. This is thought that stabilization of zirconia which is tetragonal phase for as sprayed was advanced by heat treatment.

Thus the effects of heat treatment on high hardness zirconia coating had been clarified. In this paper, the effects of thermal process (through heat treatment and plasma jet) on such high hardness zirconia coating produced at $L = 30$ mm, were investigated in detail: the

† Received on Nov. 9, 1991

* Associate Professor

** Graduate Student, Osaka University

*** Assistant Professor, College of Industrial Technology

Transactions of JWRI is published by Welding Research Institute, Osaka University, Ibaraki, Osaka 567, Japan

influence of thermal process on the Vickers hardness of the zirconia coating was clarified and the structure of the zirconia coating was discussed by using X-ray diffraction method.

2. Experimentals

The gas tunnel type plasma spraying apparatus used in this study and the experimental method to form 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 $d = 15$ mm[7].

The ZrO_2 coatings were produced under the following conditions: The power input to the plasma torch was $P = 20$ kW, and the spraying distance was $L = 30$ mm. Ar gas flow rate for gas tunnel type plasma spraying torch was $Q = 220$ l/min, and the powder feed rate was $w = 18$ g/min, the traverse speed of the substrate was $v = 96$ cm/min. In addition to 2 pass spraying, 1 pass and 3 pass spraying were carried out to obtain the coatings of different thickness.

The experiment for the plasma processing to those zirconia coatings produced was carried out under the same conditions as spraying: the power input to plasma torch was $P = 20$ kW at spraying distance of $L = 30$ mm, and the traverse speed was about $v = 100$ cm/min. The plasma processing was carried out by 6 pass scanning of coating substrate.

Table 1 shows the chemical composition and the size of zirconia powder used in this study. This zirconia powder was commercially prepared type of K-90.

The measurement of distribution of the Vickers hardness in the cross section of the zirconia 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 100 g and its load time was 25 s. The Vickers hardness was calculated as a mean value of 10 point measurement.

The X-ray diffraction method was carried out on the surface of the coating. The X-ray source was Co. The tube voltage was 20 kV and the tube current was 14 mA.

Table 1 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

For these coatings produced by 1~3 pass spraying, a heat treatment was carried out in air in a electric furnace at 800 °C for 1 hour. After heat treatment the specimens were naturally cooled in the furnace.

In order to know the change of color (brightness) of the zirconia coating formed at $L = 30$ mm when $P = 20$ kW which has gray color through thermal processing, the reflectivity of the coating surface was measured by spectrophotometer.

3. Results and Discussion

3.1 Effect of Heat Treatment on High Hardness Zirconia Coating

Figure 1 shows the distributions of Vickers hardness on the cross section of zirconia coating produced by the gas tunnel type plasma spraying, before and after the heat treatment. The measurement was carried out at each distance from coating surface in the thickness direction.

In this case, as sprayed coating was produced under the following conditions: the power input: $P = 20$ kW and the spraying distance: $L = 30$ mm. This coating was formed by twice traverse (2 pass spraying) of the powder feed rate: $w = 18$ g/min. The coating thickness was 120 μm. And as the other spraying condition, Ar gas flow rate was $Q = 220$ l/min.

In this figure, the distribution of Vickers hardness on the cross section of as sprayed zirconia coating is indicated by dotted line. From this distribution of as sprayed coating, it is found that the Vickers hardness of the coating surface layer (corresponds to the second pass)

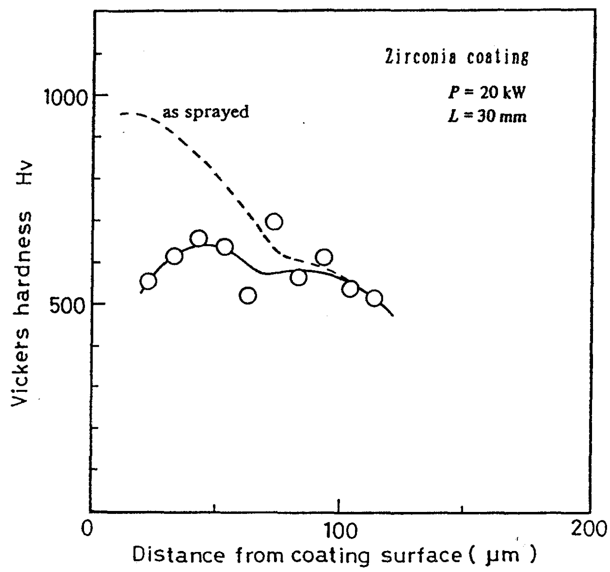

Fig. 1 Distribution of Vickers hardness on cross section of 2 pass sprayed zirconia coating after heat treatment, as sprayed: at $L = 30$mm when $P = 20$kW.

is highest value of about $H_V = 950$.

The distribution of Vickers hardness on the cross section of zirconia coating after heat treatment consists of two parabolic curves. The hardness near the substrate did not change as compared with that of as sprayed coating as shown in this figure. But the Vickers hardness near the coating surface became lower than that of as sprayed coating. The Vickers hardness of the coating was changed from $H_V = 950$ to $H_V = 650$ through heat treatment.

Figure 2 shows the distributions of Vickers hardness on the cross section of zirconia coatings produced by 1 pass spraying and 3 pass spraying respectively, before and after the heat treatment. Here Fig.2(a) is the distribution of 1 pass sprayed coating whose thickness is 70 μm, and Fig.2(b) is that of 3 pass, thick coating (180 μm).

The distributions of Vickers hardness of as sprayed coatings are also like parabolic curves. In this high hardness zirconia coating, the highest value of the hardness appears in the surface layer of the coating, namely, final pass of traverse.

After heat treatment, the Vickers hardness near the coating surface (final pass in the case of 3 pass spraying) became lower as compared with as sprayed coating. The Vickers hardness of the coating was changed from $H_V = 960$ to $H_V = 750$ for 3 pass coating, as shown in Fig.2(b).

As shown in these results of thin and thick coatings, the Vickers hardness of the surface layer of coating was lower through heat treatment, and the zirconia coating after heat treatment have a flatter distribution of Vickers hardness on the cross section. In these zirconia coatings, the value of hardness was between $H_V = 650$ and $H_V = 750$.

From the observation of these sprayed coatings after heat treatment by optical microscope, the small pores were spreadened all over the cross section of the coating. But large difference was not observed as compared with that of as sprayed coating.

3.2 Effect of Plasma Processing on High Hardness Zirconia Coating

The change of hardness distribution of zirconia coating by means of the plasma processing was also measured, and the following results were obtained.

The distribution of Vickers hardness on the cross section of zirconia coating after plasma processing is shown in **Fig. 3.** The measurement of Vickers hardness was carried out in the same manner as Fig. 1.

In this case, the coating was produced as the same conditions as Fig. 1: two pass spraying of the powder feed rate was $w = 18$ g/min at $L = 30$ mm when $P = 20$ kW. And for this coating whose thickness was 120 μm, 6 times traverse of plasma processing without powder was carried out at $L = 30$ mm when $P = 20$ kW.

In the same figure, the Vickers hardness on the cross section of as sprayed zirconia coating is indicated by dotted line.

After plasma processing, it is found that the Vickers hardness near the coating surface becomes lower than that of as sprayed coating, and the distribution of the Vickers hardness becomes flatter as well as heat treatment. Thus a high hardness layer does not exist, and the hardness at the distance from the coating surface of $l = 40$ μm is about $H_V = 680$.

Figure 4 shows the distributions of Vickers hardness on

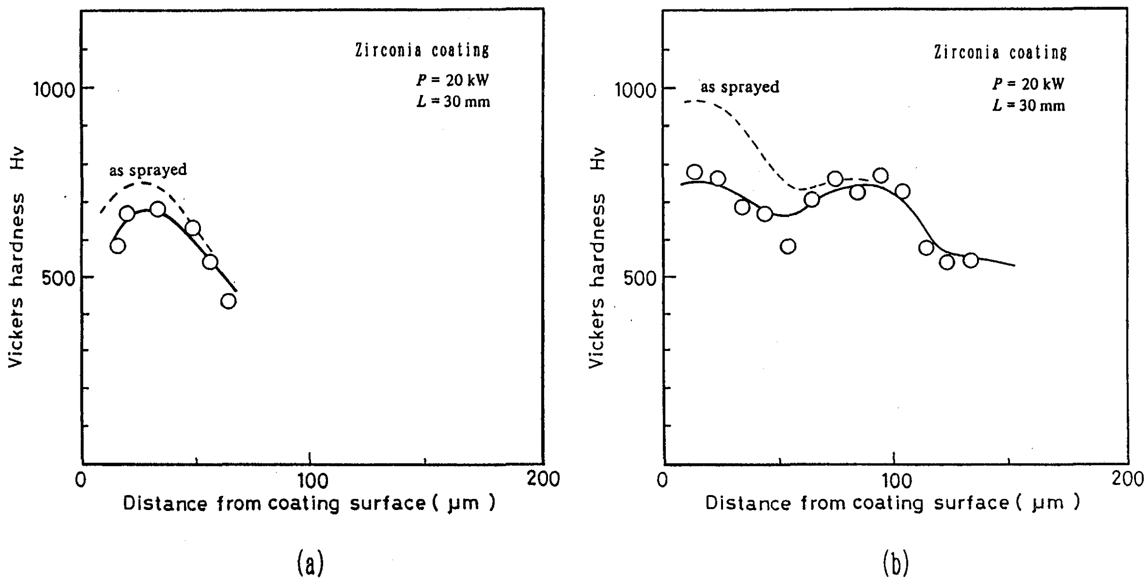

Fig. 2 Distributions of Vickers hardness on cross section of zirconia coatings after heat treatment, as sprayed: at $L = 30$mm when $P = 20$kW.
(a) 1 pass coating, (b) 3 pass coating.

the cross section of zirconia coatings produced by 1 pass and/or 3 pass spraying, before and after plasma processing. The plasma processing for these coatings was carried out at $L = 30$ mm when $P = 20$ kW, in the same manner as Fig. 2.

The coatings as sprayed were produced as the same conditions as Fig. 2: 1 or 3 pass spraying of the powder feed rate was $w = 18$ g/min at $L = 30$ mm when $P = 20$ kW respectively. In each figure of Fig. 4. the distribution of Vickers hardness of as sprayed zirconia coating was indicated by dotted line.

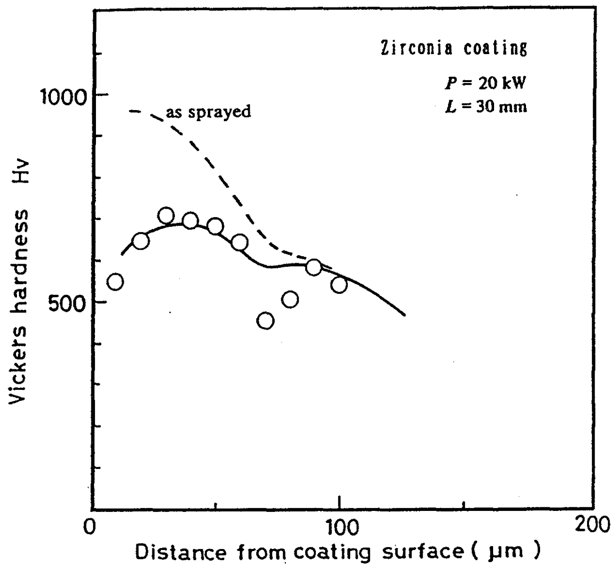

Fig. 3 Distribution of Vickers hardness on cross section of 2 pass sprayed zirconia coating after plasma processing at L = 30mm when P = 20kW.

As shown in these results in Fig. 4(a),(b), by plasma processing for 1 pass or 3 pass coating, the Vickers hardness of surface layer (final pass) is decreased as well as the case of heat treatment.

In Fig. 4 (b), for 3 pass sprayed, thick coating (180 μm) the Vickers hardness of the coating is changed from $H_V = 960$ to $H_V = 750$ by the plasma processing.

In this way, the zirconia coating after plasma processing has a flatter distribution of Vickers hardness on the cross section. And a high hardness layer does not exist in this zirconia coating, whose Vickers hardness value is about $H_V = 700$.

Thus in this high hardness zirconia coating, a high hardness layer was vanished by plasma processing. The Vickers hardness of coating after plasma processing became lower as compared with that of as sprayed coating. And the hardness distribution became flatter. Such an effect is similar to that of heat treatment.

Observing the microstructure of those zirconia coatings, it was found that the coating structure after plasma processing was almost the same structure of as sprayed coating, as well as the case of heat treatment.

3.3 Thermal Process of High Hardness Zirconia Coating

In the case of the coating after thermal processing, as mentioned above, the Vickers hardness becomes lower and the hardness distribution becomes flatter. Then, the change of Vickers hardness in the surface layer was studied.

In this high hardness zirconia coating, the highest value

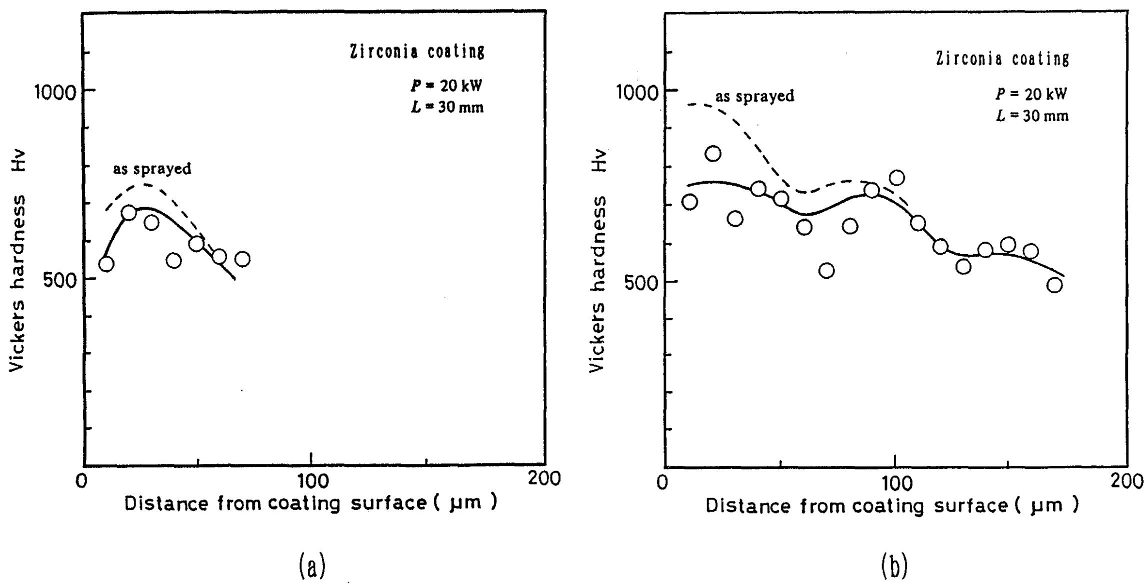

Fig. 4 Distributions of Vickers hardness on cross section of zirconia coatings after plasma processing at L = 30mm when P = 20kW.
(a) 1 pass coating, (b) 3 pass coating.

of Vickers hardness appears in the surface layer of the coating, namely, final pass of traverse.

Figure 5 shows the dependences of Vickers hardness in high hardness layer of zirconia coating on the spraying pass number at $L = 30$ mm when $P = 20$ kW. The thickness of these coatings was $t_c = 70$ μm for 1 pass coating, $t_c = 120$ μm for 2 pass coating and $t_c = 180$ μm for 3 pass coating, respectively.

Here curve A shows the Vickers hardness of as sprayed coatings, and it is found that the Vickers hardness increases as the spraying pass number increases, corresponding to the increase of coating thickness.

On the contrary, curve B shows the Vickers hardness of the coating after thermal processing (heat treatment and plasma processing) and the value of H_V is low as compared with as sprayed coating. For the spraying pass number, the dependence of Vickers hardness is weak. The values of Vickers hardness are between 650 and 750, and almost same values for both thermal processings.

The changes of Vickers hardness in the high hardness layer of zirconia coating after thermal processing are shown in **Fig. 6**. Both coatings after heat treatment and plasma processing were the same coatings as that shown in Fig. 1 and Fig. 2, respectively. As sprayed coating was produced by 2 pass spraying at $L = 30$ mm when $P =$ 20kW.

The hardness of as sprayed coating becomes lower value through heat treatment and plasma processing. The both values are almost the same: $H_V = 680$ and $H_V =$ 700. But in the case of heat treatment, a little low value can be obtained.

Now, after heat treatment of these zirconia coatings produced at $L = 30$ mm when $P = 20$ kW, the color of the coating was changed from gray to yellow, because of the oxidization. Then, to know the brightness of coating surface, the reflectivity was measured by the spectrophotometer.

Figure 7 shows the changes of reflectivity of zirconia coating after thermal processing. This coating was produced by 1 pass spraying at $L = 30$ mm when $P = 20$ kW.

The reflectivity of as sprayed coating is $R = 22\%$. On the other hand, after plasma processing the reflectivity is $R = 52\%$ and after heat treatment, $R = 63$ %. Thus, both thermal processings have the same effect on the reflectivity of coating surface. This characteristic of

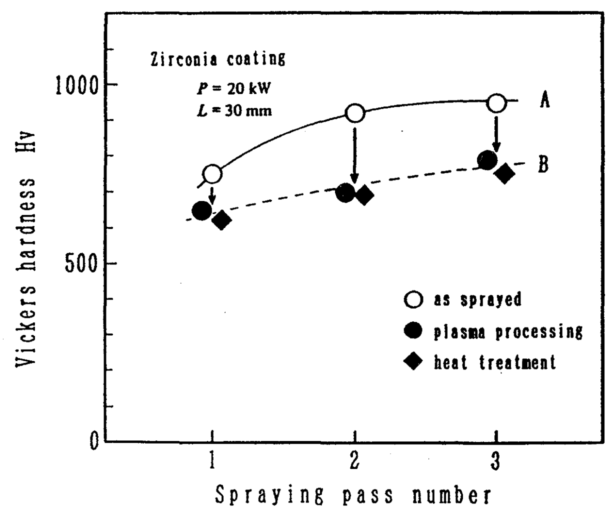

Fig. 5 Dependences of Vickers hardness of zirconia coating on spraying pass number at L = 30mm when P = 20kW, A: as sprayed, B: thermal processing.

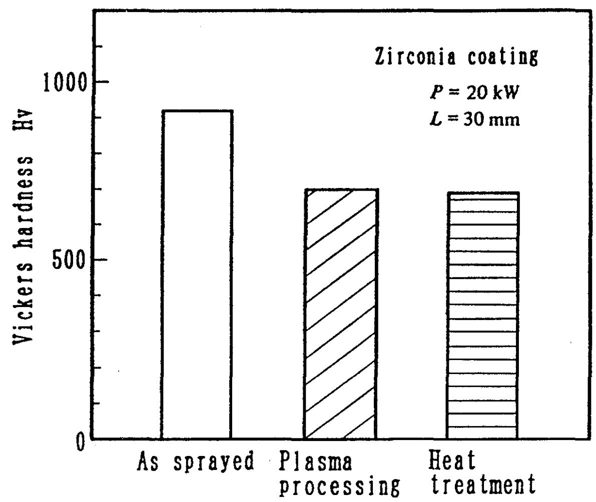

Fig. 6 Changes of Vickers hardness of zirconia coating after thermal processing; 2 pass sprayed at L = 30mm when P = 20kW.

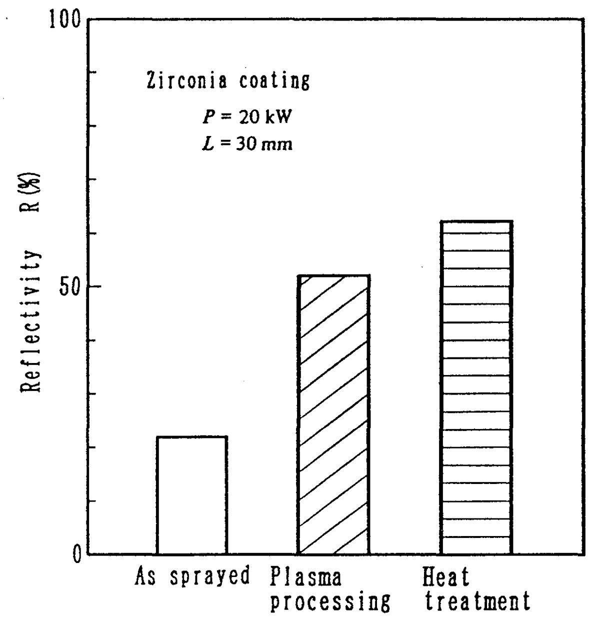

Fig. 7 Changes of reflectivity of zirconia coating after thermal processing; 1 pass sprayed at L = 30mm, when P = 20kW.

reflectivity is similar to that of Vickers hardness described above.

3.4 Angular Separation of Tetragonal Peaks of zirconia sprayed coating

From the X-ray diffraction patterns of the surface of high hardness zirconia coating formed by the gas tunnel type plasma spraying, two peaks of tetragonal ZrO_2 near the degree of 40° are sub peak of 40.7° and main peak of 41.1° respectively. These two peaks obtained from (002) and (200) planes.

Through heat treatment two peaks separated in the diffraction angle and became clearer than that of as sprayed coating. But the crystal form of this zirconia coating (tetragonal ZrO_2) did not change before and after heat treatment.

Figure 8 shows the changes of angular separation between two ZrO_2 peaks from (002) and (200) planes of the surface of zirconia coating after thermal processing. This coating was produced by 2 pass spraying at $L = 20$ mm when $P = 20$ kW.

As compared with the angular separation of $\Delta 2\theta = 0.35°$ of as sprayed coating, the coating after plasma processing has a little larger angular separation of $\Delta 2\theta = 0.36°$. This shows that the structure of the zirconia coating did not change largely through plasma processing. Because the processing time was very short, a few seconds.

On the other hand, the angular separation of the coating after heat treatment is broader than that after plasma processing. The angular separation between the two tetragonal peaks was changed from $\Delta 2\theta = 0.35°$ to $\Delta 2\theta = 0.39°$.

Thus, the angular separation between the two tetragonal peaks from (002) and (200) planes was broader through thermal process. It is thought that the crystal form of zirconia which is tetragonal phase for as sprayed was stabilized by the thermal process.

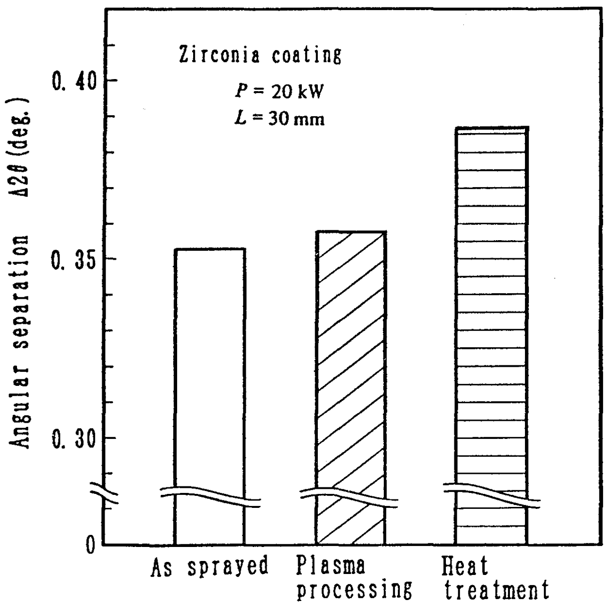

Fig. 8 Changes of angular separation between two ZrO_2 peaks of X-ray diffraction patterns of the surface of zirconia coating after thermal processing; 2 pass sprayed at $L = 30$mm, when $P = 20$kW.

4. Conclusion

According to the measurement of the distribution of the Vickers hardness of the zirconia coating by means of gas tunnel type plasma spraying, the hardness of high hardness layer near the surface became lower after the heat treatment. The same result was obtained by plasma processing of as sprayed coating.

For two pass coating, Vickers hardness of as sprayed zirconia coating was $H_V = 950$ at $L = 30$ mm, when $P = 20$ kW. After thermal process, H_V becomes the lower value of about $H_V = 680$.

When the spraying pass number was larger, the Vickers hardness of the high hardness layer was higher: Vickers hardness was about 1000 for 3 pass sprayed coating. And after thermal processing for those coatings (1~3 pass sprayed), the Vickers hardness of each coating became to lower value of $H_V = 650 \sim 750$ which was independent of the spraying pass number.

Both thermal processings (heat treatment and plasma processing) had similar effect on the characteristic of the Vickers hardness. For example, H_V of 2 pass sprayed coating was between 650 and 700, and almost the same value for both thermal processings.

Corresponding to the change of color of this coating from gray to yellow after heat treatment, the reflectivity of as sprayed coating, $R = 22$ % was changed largely: after plasma processing the reflectivity was $R = 52$ % and after heat treatment, $R = 63$ %. Thus, both thermal processings had the same effect on the reflectivity of coating surface. This characteristic of reflectivity was similar to that of Vickers hardness.

The results obtained by means of the X-ray diffraction method showed that the crystal form of this zirconia coating which is tetragonal ZrO_2 was not changed by the heat treatment and plasma processing.

After heat treatment the angular separation between two tetragonal peaks from (002) and (200) planes was broader. On the other hand, through plasma processing, the angular separation between the two tetragonal peaks was a little broader. From this result, it is thought that the stabilization of the crystal form of zirconia (tetragonal phase) needs more time than a few seconds of plasma processing.

Acknowledgement

This study was financially supported in part by a Grant-in-Aid for Scientific Research from the Japanese Ministry of Education, Science and Culture.

References

1) Y.Arata, A.Kobayashi, Y. Habara and S. Jing; Trans. JWRI **15**-2 (1986) 237
2) Y. Arata, A. Kobayashi and Y. Habara; J. High Temp. Soc., **12**-2 (1987) 116 (in Japanese)
3) Y. Arata, Y. Habara and A. Kobayashi; Trans. JWRI. **16**-1 (1987) 21
4) Y. Arata, Y. Habara, S. Kurihara and A. Kobayashi; Trans. JWRI, **16**-2 (1987) 255
5) A. Kobayashi, N. Hasegawa and H. Namikawa; Trans. JWRI, **18**-1 (1989) 12
6) A. Kobayashi, N. Bessho and M. Higuchi; Trans. JWRI, **19**-2 (1990) 117
7) A. Kobayashi, K. Yamahuji and T. Kitamura; Trans. JWRI, **20**-1 (1991) 47
8) N. Iwamoto, N. Umesaki and S. Endo; Fine Ceramics, **6** (1985) 120
9) R.A.Miller, J.L.Smialek and R.G.Garlick; Advances in Ceramics, Am. Ceram. Soc., Vol.2 (1981) 241