Improvement of Plasma- Sprayed ZrO_2 Coatings by Cr_2O_3 Penetration and Evaluation of Cavitation Erosion †

Akira OHMORI* and Kunihiko OGINO**

Abstract

As plasma sprayed ZrO_2 coatings, like all ceramics coatings, include micro cracks and non-bonded part between flattened ZrO_2 particles, such properties as mechanical strength , wear resistance, cavitation erosion are greatly reduced. The possibility of improving the cavitation erosion of ZrO_2 coatings by penetration treatment with Cr_2O_3 was examined. It was found that the hardness of ZrO_2 coatings penetrated with Cr_2O_3 increased greatly, compared with as-sprayed ZrO_2 coatings. The evaluation of cavitation erosion of ZrO_2 coatings was investigated by magnetostrictive cavitation tests at a frequency of 20 kHz and at a horn amplitude of 50μm .The cavitation erosion property was improved greatly by Cr_2O_3 penetration treatment of the ZrO_2 coating.

KEY WORDS : (Plasma-spray) (ZrO_2) (Coating) (Cr_2O_3) (Sintering) (Erosion) (Cavitation) (Penetration)

1. Introduction

Coatings formed by plasma spraying, etc. have uncombined portions and cracks. These can be penetrated by the solvent method but coatings treated by this method generally cannot withstand cavitation for long times under severe conditions of ultrasonic vibration. It is also reported that fusion/thermal diffusion and mechanical compaction methods[1-2] and coating bond improving methods[3-5] of plating uncombined portions with Cu or filling pores with Cr_2O_3 are in use.

The penetration method to fill pores and microcracks in coatings with Cr_2O_3 prevents the propagation and growth of cracks under stress condition and increases corrosion resistance in corrosive environments by preventing liquid from infiltrating into pores and cracks.

Wear rates and the mercury method are used to evaluate coating structures and properties[3] but ultrasonic vibration has hardly been used for evaluating damage to thermal sprayed coatings up to the present. In such circumstances an attempt was therefore made to fill pores and cracks of sprayed ZrO_2 coatings with Cr_2O_3 , heat treat the coatings and subject them to cavitation tests.

As a result, cavitation erosion was reduced significantly. The test results are reported.

2. Experimental procedure

Test specimens were prepared by plasma-coating 16 mm (0.63in)-diameter steel bars with a 500 μm thick ZrO_2 layer. The specimen was penetrated as shown in the flowchart of **Figure 1**. Specifically it is immersed in CrO_3 liquid and burned to fill uncombined portions of ZrO_2 and pores with Cr_2O_3 which is converted from Chromic anhydride CrO_3 (which has the highest production rate of Cr_2O_3 of chromates).

$$CrO_3 \rightarrow 1/2\,Cr_2O_3 + 3/4\,O_2 \qquad (1)$$

It is reported that CrO_3 is converted to Cr_2O_3 via Cr_3O_8 and Cr_2O_5 according to quation (1) at a temperature over 673K.

The specimen was immersed in chromic anhydride CrO_3 for 40 sec heated to 723K for 60 min in an electric furnace open to the atmosphere and cooled down in the furnace. This immersion and heating process was repeated eight times. Specimens with a Cr_2O_3 production of about 8 mg/cm^2 were adopted for testing[4].

The cavitation tester used is the magnetostrictive vibration type and has a high-frequency power of 1.2 kW and a resonance frequency of 19.5 ± 0.5 kHz. The vibration amplitude used in the test was kept constant at 50 μm. The amplitude was measured with a noncontact displacement

† Received on November 29, 1999
* Professor
** Lecturer, Kinki University, Higashiosaka

Transactions of JWRI is published by Joining and Welding Research Institute of Osaka University, Ibaraki, Osaka 567-0047, Japan.

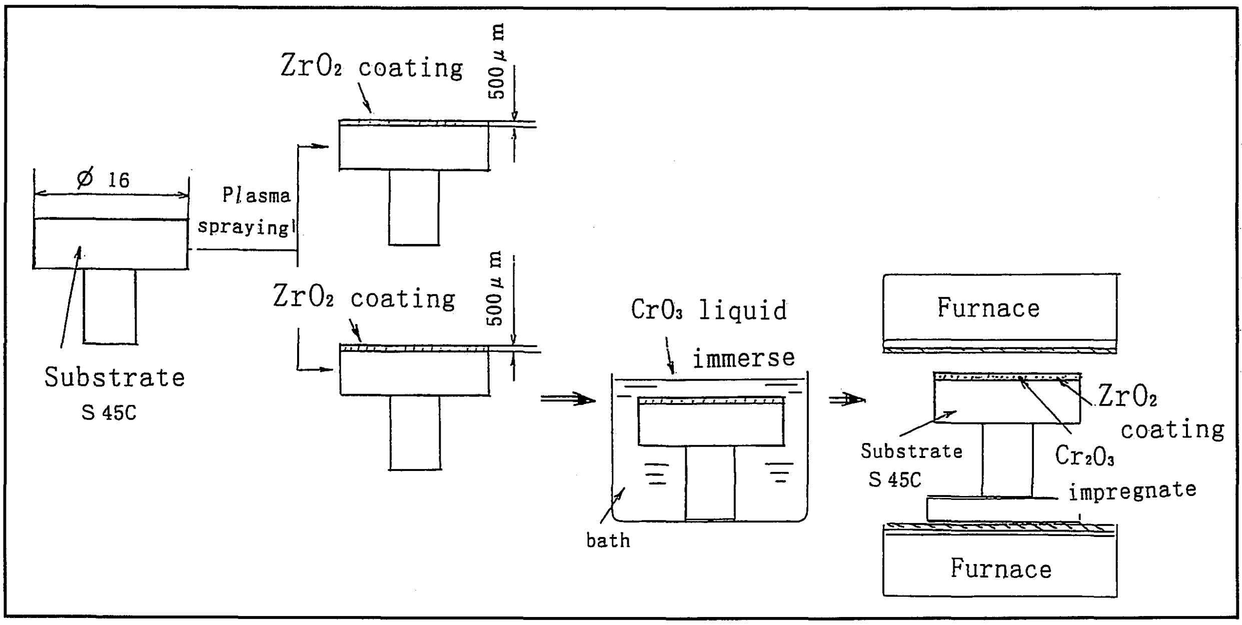


Fig. 1 Dipped in CrO_3 solution to penetrate,then baked to melt CrO_3 and impregnate the uncombined part of ZrO_2 as diagrammatically illustrated.

Table 1 Chemical compositions and size of powders.

Material	composition (wt%)					Size
	ZrO_2	YO_3	Al_2O_3	SiO_2	Fe_2O_3	(μm)
ZrO_2-8%Y_2O_3	—	8.36	0.02	0.09	0.07	10~45

meter and a dial gauge. As shown in Fig. 1 an unsealed specimen namely a 16 mm (0.63 inch) -diameter steel bar with ZrO_2 coating and a penetrated specimen, whose uncombined ZrO_2 portions and pores were filled with CrO_3 and burned were mounted on the vibrator with screws. Distilled water was used as the testing water and kept at 293 ± 2K. Spray ZrO_2 powder, including 8% Y_2O_3 by weight, was used for spraying.

The composition of the powder is shown in **Table 1**.

3. Results and discussion

3.1 Relationship between erosion and elapsed time

Figure 2 shows the relationship between erosion and elapsed time. When an unsealed specimen as sprayed was compared with a specimen penetrated with Cr_2O_3, the erosion of the latter was reduced to one fourth of that of the former. The Cr_2O_3 - penetrated specimen showed no remarkable change in the roughness of the eroded surface. In **Figure 3** the sprayed surface of the unsealed specimen in (a) is compared with that of the Cr_2O_3 penetrated one in (b) by using SEM observation.

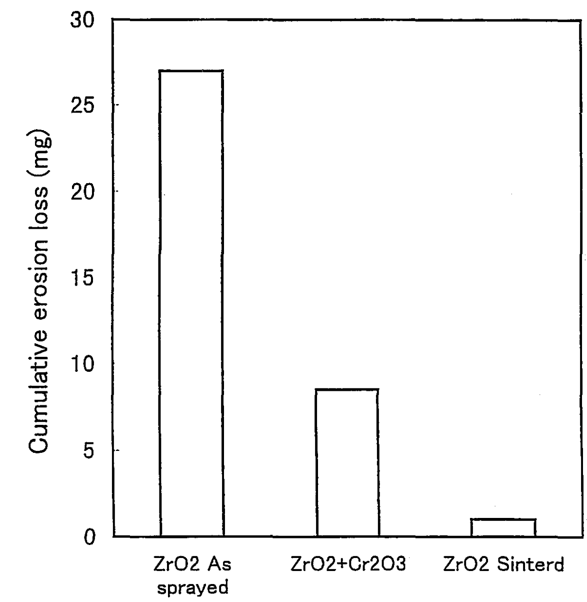


Fig. 2 Growth of cavitation erosion as a function of time.

There are many cracks about 25 μm long and about 0.3 μm wide traversing layered flat particles in (a) and also a lot of cracks in all directions in (b)[2] thus revealing remarkable difference between (a) and (b) in SEM image. The Cr_2O_3 - penetrated specimen tended to be tinged with a dark tone of color due to the heating effect.

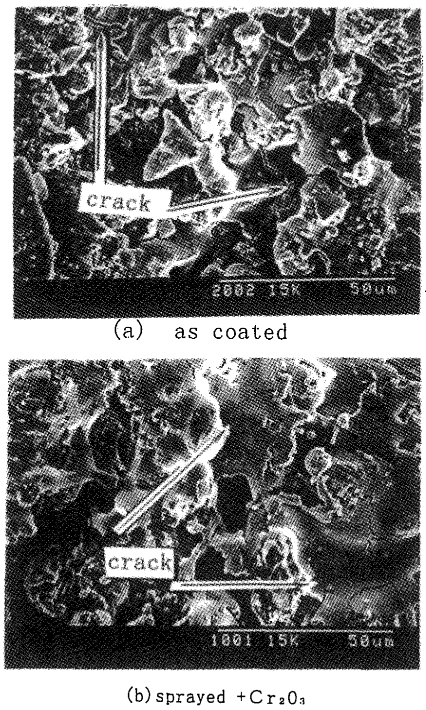


Fig. 3 SEM images of (a) as sprayed and (b) impregnated surfaces of thermal sprayed coatings.

3.2 EPMA analysis of portions filled with Cr_2O_3

An SEM observation of the cross section of portions filled with Cr_2O_3 is shown in **Figure 4** (a), a ZrK_α characteristic X-ray image in (b) and a CrK_α characteristic image in (c). As shown in (c), it is suggested that Cr is present between layered flat particles and in boundaries in all directions [5]. **Figure 5** presents an EPMA line analysis of Cr_2O_3 having infiltrated into ZrO_2 coating. The almost continuous detection of Cr_2O_3 in (b) proves that the penetrating treatment filled layered flat particle boundaries with Cr_2O_3. **Figure 6** shows SEM images of the surface of layered flat particles. Fig. 6 (a) indicates flat particles as large as about 50 μm on the initial surface. Fig. 6 (b), showing a CrK_α characteristic X-ray image, proves that Cr is present in particle boundaries and especially pores .

Fig. 6 (c) and (c)' present ZrK_α characteristic X-ray images. Fig. 6 (a)' indicates that only 10 min after the test started, due to the action of cavitation impingement, particles began to be broken down in boundaries while large flat particles were reduced in size, and tended to become smaller on average. Fig. 6 (b)', presenting a CrK_α characteristic X-ray image, demonstrates that, though 10 min passed since cavitation had occurred, Cr remained without being removed by breakage, thereby preventing large eroded particles from being separated. The Cr_2O_3 penetration was proved to produce a significant effect on the decrease of erosion. **Figure 7** shows changes in hardness in relation to penetration with Cr_2O_3.

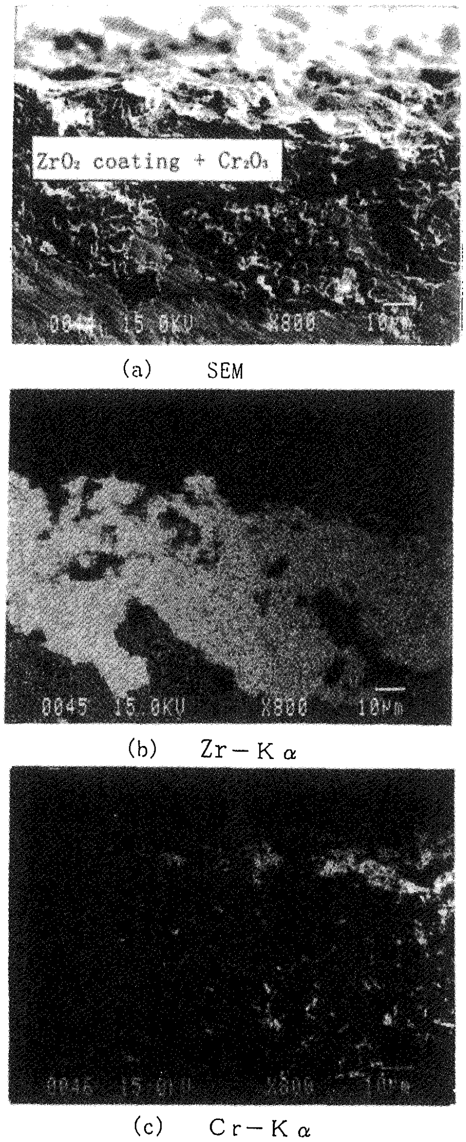
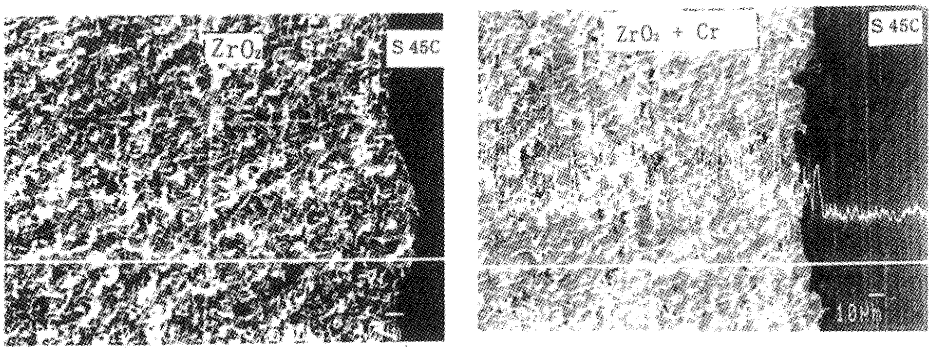


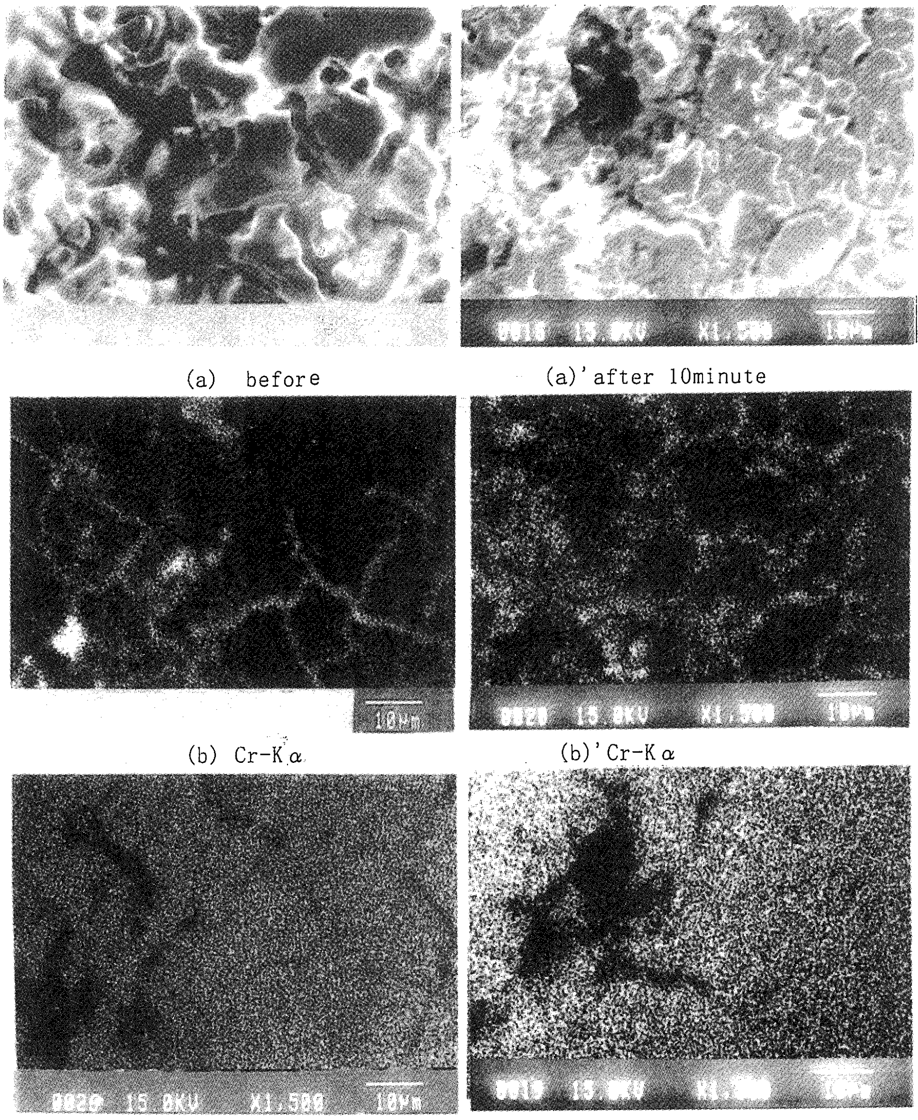
Fig. 4 Section of Cr_2O_3 - filled specimen taken (a) in SEM and with characteristic X-rays of (b) $Zr\text{-}K_\alpha$ and (c) $Cr\text{-}K_\alpha$.

The ZrO_2 coating penetrated with Cr_2O_3 in (b) was 50% harder than the unsealed ZrO_2 coating in (a). This is supposed to be due to the formation of a dense Cr_2O_3 layer [6]. It is considered that this effect produces a delay of the crack propagation and abrasion.



(a) as-coating (b) impregnated Cr

Fig. 5 EPMA line analysis for (a) as sprayed and (b) Cr_2O_3 - filled samples.



(c) Zr－Kα (c)' Zr－Kα

Fig. 6 SEM before image (a) , after 10 minute (a)', characteristic X-ray image with Cr-K_α, (b). (b)',(c) and (c)' show the images taken with Zr-K_α .

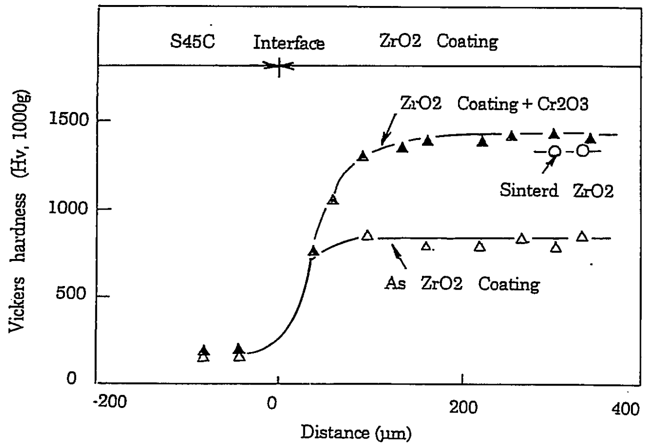


Fig. 7 Vickers hardness distribution of cross-section of ZrO_2 coating as-sprayed, heat-treatment with Cr_2O_3 - filled and sintered zirconium.

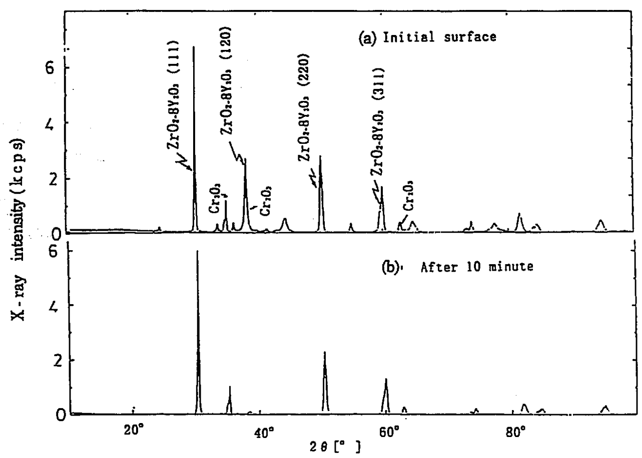


Fig. 8 XRD for the sprayed ZrO_2 coating (1) before and (2) after 10 minutes of the erosion test.

3.3 X-ray diffraction of eroded ZrO_2 spray coating

Figure 8 illustrates the X-ray diffraction pattern of the eroded surface of sprayed ZrO_2 coating before (1) and after the erosion (2). No remarkable change can be found at the diffraction angle of θ even when comparison is made before the erosion starting and 10 min after it. There was a tendency for X-ray intensity (cps) to decrease in the profile 10 min after the erosion. This is supposed to be due to the disorder of sprayed ZrO_2 coating crystals as a result of being subjected to severe cavitation, specifically repeated Hertzian stress and stress due to cavitation impingement[7]. **Figure 9** presents a model for the erosion of the layered flat particle portion of a sprayed ZrO_2 coating due to ultrasonic vibration. A process is macroscopically analyzed in

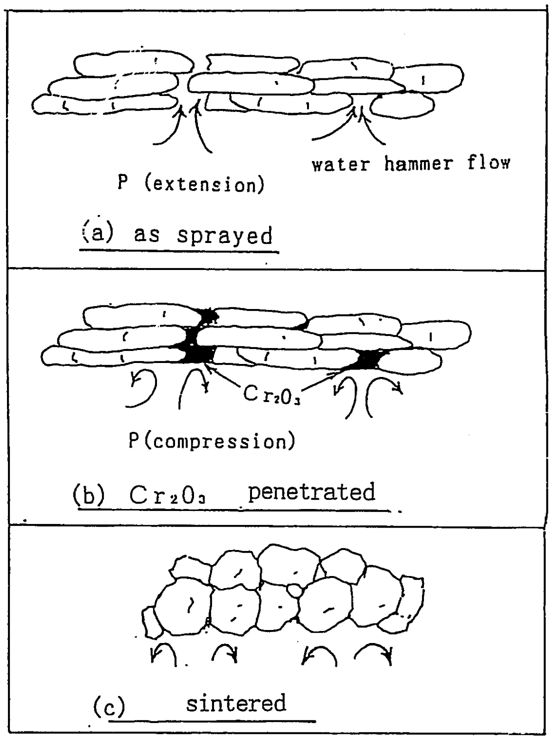


Fig. 9 Mechanism model for the erosion that may proceed under ultrasonic vibration of sprayed ZrO_2 in the layer of flattened particles.

which a specimen in (a) hits the liquid surface in accordance with cavitation vibration when the vibrator descends. Then, a water hammer force P (compressive force) acts on the whole surface of the specimen and exercises a breaking effect due to Hertzian stress on layered particle boundaries, particle junctions, uncombined particles, microcracks and pores. It is supposed that the penetrating effect of Cr_2O_3 on uncombined portions and microcracks was effective in preventing the above stress effects in (b). For the above reasons, the penetrating treatment using Cr_2O_3 prevents the propagation and growth of cracks under various stress conditions and contributes to the increase of corrosion resistance by preventing corrosive liquid from infiltrating into pores and cracks. Thus, it was proved that the penetrated specimen was the propagation and growth of cracks under various stress conditions and contributes to the increase of corrsoion resistance by preventing corrosive liquid from infiltrating into pores and cracks. Thus, it was proved that the penetrated specimen was improved about 70% in cavitation resistance as compared with the unsealed one.

4. Conclusions

Thermal sprayed ZrO_2 coatings generally contain pores and microcracks. The pores and microcracks can be filled with Cr_2O_3 by penetrating treatment, thus making it possible to produce a denser sprayed coating. The properties of the Cr_2O_3 layer was evaluated and the following conclusions were obtained. Penetrating treatment using Cr_2O_3 can fill densely pores, microcracks and uncombined portions with Cr_2O_3. The penetrated ZrO_2 coating was about 50% harder than the unsealed one. The sprayed ZrO_2 coating penetrated with Cr_2O_3 was about 70% higher in cavitation resistance than the unsealed one.

Acknowledgement

The authors would like to express their sincere appreciation to Dr. Y. Harada (Tocalo Co.,Ltd.) for providing test pieces.

References

1) A. Ohmori, New Development of Thermal Spraying, High temperature society of Japan, Vol. 16, supplement, 1990, p.224.
2) Y. Arata, A. Ohmori and Chng-Ju Li, Structure and Property of Plasma Sprayed Alumina Coatings, High Temperature Society of Japan, Vol. 14, 1998, p.220.
3) K. Nomura, K. Komatu,Y. Harada , K. Nakahira and I. Oki, Surface Finishing Society of Japan, 1990, p.149.
4) A. Ohmori, Z. Zhou and K. Inoue, Liquid Sintering of Plasma Sprayed ZrO_2 Coating Microstructure by Penetration Treatment of Liquid Mn Alloy Coating in Gas Atmosphere, High Temperature Society of Japan, Vol. 23, supplement, 1998, p.230.
5) K. Ogino, A. Hida, A. Ohmori and I. Okamoto, Cavitation Erosion of alumina Ceramics Coated by Plasma Splay, High Temperature Society of Japan, Vol. 19, 1993, p.88.
6) K. Ogino, A. Ohmori and J. Morimoto, Erosion characteristics of ZrO_2 coating, its improvement by penetration of Cr_2O_3, the Journal of the Surface Finishing of Japan, Vol. 50 , 1999, p.99.
7) A. Ohmori and K. Ogino, Evaluation of Cavitation Erosion of ZrO_2 Coating Penetrated with Cr_2O_3, High Temperature Society of Japan, Vol. 24, Supplement, 1999, p.222.