# Crystal and micro structures of plasma sprayed yttrium oxide coatings by axial injection of fine powder slurries

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Yttrium oxide ($Y_2O_3$) coatings have been prepared with high power axial injection plasma spraying using fine powder slurries. It is clarified that the coatings have high hardness, low porosity and high erosion resistance against $CF_4$ contained plasma in the previous study. This suggests that the plasma spraying of $Y_2O_3$ with slurry injection techniques is applicable to fabricating equipments for semiconductor devices, such as dry etching. Surface morphologies of the slurry coatings with splats are almost similar to conventional plasma-sprayed $Y_2O_3$ coatings, identified from microstructural analysis by field emission SEM in this study. However, no lamellar structure has been seen from cross sectional analysis, which is apparently different from the conventional coatings. It has also been found that crystal structure of the slurry $Y_2O_3$ coatings mainly composed of metastable phase of monoclinic structure, whereas the powders and the conventional plasma spray coatings have stable phase of cubic structure. Mechanism of coating formation by plasma spraying with fine powder slurries will be discussed based on the findings.

## 1 Introduction

The size of semiconductor and flat-panel-display (FPD) production equipment for dry etching, sputtering and ashing has been increasing due to the increased size of Si wafer and the FPD, where plasma treatment is effectively used for micro~nano fabrication especially in dry etching. Applied power for generating plasma is also increasing to fabricate the Si and LCD devices uniformly onto the large scaled substrates and to make high etching rate for cost reduction. This trend strongly promotes application of plasma sprayed coatings by high-purity ceramics for anti-plasma erosion at inside wall of the chamber and for high electric strength (high breakdown voltage) of electrostatic chuck (ESC) to replace from conventional techniques, such as anodized aluminum (alumite film) and sintered bulk ceramics [1, 2]. For example, inner diameter of the chamber wall is increasing from 400 to 600 mm in the Si device production equipment due to the enlargement of the wafer size.

It has been difficult to use the alumite film as a shield or an ESC to protect the chamber parts because the halogen contained plasma with high power erodes the film with high rate. This intense erosion generates a large amount of particles and results in frequent maintenance of the production equipment and decrease of yield ratio of the devices due to deposition of the particles. Sintered bulk ceramics has been also difficult to use as the shielding parts by the enlargement of the equipment because production of large scaled ceramics is difficult technically and its cost tends to become high.

Plasma sprayed ceramic coatings have technical and commercial advantages to overcome the problems, such as no limitation of the equipment size, relatively higher anti-plasma erosion resistance, higher breakdown voltage and relatively low cost to make thick coating of about a few hundred micro-meters. As ceramic materials for plasma spraying, aluminum oxide (alumina, $Al_2O_3$) and yttrium oxide (yttria, $Y_2O_3$) have been utilized presently due to its high durability against the halogen contained plasma [2, 3]. In particular, spraying technique seems to be better for $Y_2O_3$ because of its high brittleness and high cost.

Recent systematic studies by Kitamura et al. have revealed that plasma-sprayed $Y_2O_3$ coatings have higher plasma erosion resistance than $Al_2O_3$ coatings as well as sintered bulk $Al_2O_3$ against $CF_4$ containing plasma at the actual conditions in semiconductor fabrication processes [4, 5]. The studies also have found that sintered bulk $Y_2O_3$ is still superior to plasma spray coatings in terms of the plasma erosion resistance and retention of smoother eroded surface.

Although the studies clarify use of agglomerated-and-sintered $Y_2O_3$ powder consisting of large primary particle of about 5 μm is effective for producing highly anti-plasma erosion resistance retaining smooth surface, which may prevent generation of large-sized particles, the surface roughness is still higher than the bulk [5, 6]. The inferiority of the $Y_2O_3$ coating of erosion resistance and rough eroded surface shows that further improvement is still required for plasma spray coating.

Denser $Y_2O_3$ coatings are considered to be one of the solutions to improve these properties, such as plasma erosion resistance and smooth eroded surface. Using finer powders less than 10 μm has been found to be effective to prepare denser coatings with thinner lamellae splats compared to traditionally sized powders [7, 8]. By suspending the fine powders in liquid and injecting the solid/liquid slurry into the plasma plume, a reliable delivery mechanism to spray fine particles to achieve dense coating structures can be obtained. [9, 10].

In previous study, $Y_2O_3$ coatings have been prepared with high power axial injection plasma spraying using fine powder slurries [11]. The slurry $Y_2O_3$ coatings have shown high density, uniform structure, high hardness, high plasma erosion resistance and retention of smoother surface after plasma erosion. In this paper, crystal and micro structures of the slurry $Y_2O_3$ coatings have been studied. Mechanism of coating formation by plasma spraying with fine powder slurries has been also discussed based on the findings.

## 2 Experimental

### 2.1 Spray Powders and Slurries

Three types of $Y_2O_3$ powders were prepared by Fujimi Inc. (Kakamigahara, Gifu, Japan) in this study: DTS-Y27-63/10 (Y-c: $d_{50}$ ~ 37 μm, agglomerated-and-sintered, conventional), DTS-Y34 (Y-f5, $d_{50}$ ~ 5 μm) and DTS-Y35 (Y-f1, $d_{50}$ ~ 1 μm). Average powder diameters of $d_{50}$ were estimated using laser diffraction and scattering method (LA-300, Horiba Co. Ltd., Kyoto, Japan). The conventional sized powder (Y-c) and Y-f1 were fed to plasma torch by conventional method. Slurry feeding was carried out for other two fine powders. Based on the slurry optimization, the slurry solid concentration was set at 10 wt.% in ethanol based solvent Sintered-bulk $Y_2O_3$ (Y-bulk), which were prepared by Fujimi Inc., were used as a reference material.

### 2.2 Preparation of the Plasma Spray Coatings

Table 1 summarizes specimens prepared in this study with feedstock and plasma spray conditions. Atmospheric plasma spraying by SG-100 (Praxair, Cincinnati, OH, USA) with Y-c was used to prepare a conventional coating of Y-c-c. The conditions are summarized in Table 2. Axial III$^{tm}$ (Northwest Mettech Corp., North Vancouver, BC, Canada) was used for producing high power plasma spray coatings of Y-c-ha, Y-f1-hb, Y-f2-hb and Y-f2-hc, as summarized in Table 3. The Nanofeed$^{tm}$ Model M650 Liquid Powder Feeder (Northwest Mettech Corp.) was used to deliver fine micron powders in a slurry form into the plasma plume. The Nanofeed 650$^{tm}$ is a new device that precisely feeds slurry mixtures using mass flow control of both slurry and atomizing gas to provide uniform atomizing at the injector.

**Table 1.** $Y_2O_3$ specimens used in this study with feedstock and spray conditions for the coatings.

| Coating | Pow-der | $d_{50}$ [μm] | Plasma gun | Powder feeding | Spray Conditions |
|---|---|---|---|---|---|
| c-c | Y-c | 37 | SG-100 | Conven-tional | Table 2 |
| c-Ax | | | Axial III$^{tm}$ | | Table 3(a) |
| f5-Ax | Y-f5 | 5 | | | Table 3(b) |
| f5s-Ax-Ar | | | | Slurry | Table 3(c) |
| f1s-Ax-Ar | Y-f1 | 1 | | | |
| f1s-Ax-N | | | | | Table 3(d) |
| Bulk | Sintered $Y_2O_3$ (15 × 15 × 2$^t$ mm) | | | | |

Substrates of aluminum alloy (A6061, 50 × 70 × 2.0$^t$ mm$^3$) were sand blasted by alumina grit prior to plasma spraying. Surfaces of sprayed coatings cut to 15 × 15 × 2.0$^t$ mm and sintered $Y_2O_3$ were mirror-polished using colloidal silica with an average diameter of 0.06 μm to study both the durability against the $CF_4$ containing plasma and the erosion mechanism in detail for the plasma erosion test described below.

**Table 2.** Conditions of conventional spraying (SG-100).

| Parameters | Conditions |
|---|---|
| Ar/He flow rate (L/min) | 39/7.9 |
| Power (kW) | 32 |
| Powder feeding rate (kg/h) | 0.9 |
| Spray distance (mm) | 120 |

**Table 3.** Conditions of high power spraying (Axial III$^{tm}$).

| Parameters | Conditions | | | |
|---|---|---|---|---|
| | (a) | (b) | (c) | (d) |
| $Ar/N_2/H_2$ flow rate (L/min) | 90/54/36 | 75/5/20 | 168/23/29 | 81/81/18 |
| Power (kW) | 96 | 90 | 83 | 88 |
| Powder feeding rate (kg/h) | 3 | 1 | - | |
| Slurry feeding rate (kg/h) | - | | 1 | 2 |
| Spray distance (mm) | 100 | | 50 | |

### 2.3 Evaluation of Plasma Erosion Test

Conditions of the plasma erosion tests are summarized in Table 4. Before introducing into the reactive ion etching (RIE) chambers, the surface of the mirror-polished specimens was partially masked by polyimide tape outside. Then, eroded area was center around 5 × 5 mm$^2$. The erosion rate was estimated by measuring the step height between masked area and eroded area using stylus method (SV-3000CNC, Mitsutoyo Corp., Kawasaki, Kanagawa, Japan). Possibility to generate large sized particle was discussed through micro-structural analysis of the eroded surface by SEM and the stylus method.

**Table 4.** Conditions of the plasma erosion test.

| RIE equipment | | NLD-800 (ULVAC) |
|---|---|---|
| Parameters | | Conditions |
| $Ar/CF_4/O_2$ flow rate (L/min) | | 0.095/0.0095/0.001 |
| Chamber pressure (Pa) | | 1 |
| Plasma power (W) | | 400 |
| Exposure area (mm) | | 100φ |
| Exposure time (min) | | 52.5 |
| Exposure cycle (min) | Exposure | 0.5 |
| | Interval | 3 |

### 2.4 Evaluation of Coating Properties

Scanning electron microscopies (SEM) were carried out for microstructural analysis. Porosities of the coatings were estimated by image analysis from optical micrographs. Micro Vickers hardness was measured with load and loading time of 200 gf and 10s, respectively. Crystal structures of the powders and the coatings were identified from X-ray diffraction analysis (XRD: ULTIMA IV, RIGAKU Corp., Japan).

## 3 Results and discussion

### 3.1 Plasma erosion properties

Erosion rates of the $Y_2O_3$ coatings and bulk are shown in Fig. 1 against $Ar/CF_4/O_2$ plasma. All coatings prepared by Axial III$^{tm}$ have higher erosion resistance than the conventional coating and are inferior to bulk $Y_2O_3$. Use of fine powder with dry feeding seems to have little effect on increasing the resistance when comparison with c-Ax and f5-Ax. Slurry coatings show higher resistance than dry fed coatings: c-c, c-Ax and f5-Ax. In particular, using finer powder of 1 μm (Y-f1) seems to obtain better properties than 5 μm. Erosion rates of the slurry coatings by Y-f1 powder were approximately 65 nm/min, which was 0.8 times less than that of the c-c coating (85 nm/min) and was about 1.4 times higher than that of the bulk $Y_2O_3$ (45 nm/min). As the c-c coating is similar to the coatings utilized in actual production equipments, it can be considered that lifetime is extended about 1.2~1.3 times when applying the slurry coating.

Previous study [6] has reported that no improvement of the erosion resistance is seen when changing primary particle size of $Y_2O_3$ in agglomerated-and-sintered powders, which is almost similar to the c-c. This suggests slurry feeding of fine $Y_2O_3$ powders, axial injection of the slurry and high power plasma spraying, which are conducted in the study, are quite effective to improve the coating properties, such as decreasing porosity and increasing hardness, as well as increasing plasma erosion resistance.

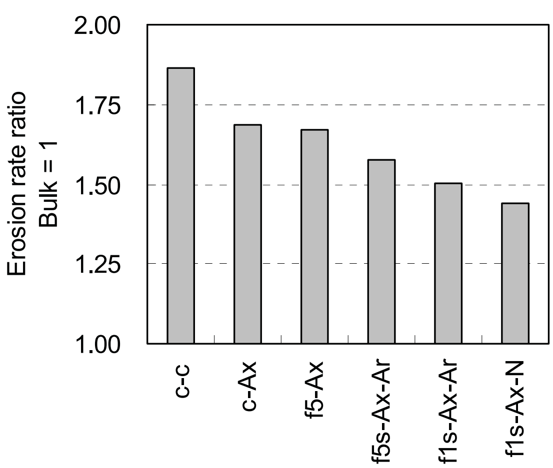


**Fig. 1.** Erosion rate ratio of the $Y_2O_3$ coatings against $Ar/CF_4/O_2$ plasma, bulk as a reference.

### 3.2 Surface morphologies after the plasma erosion test

Figure 2 shows SEM images of the surfaces of after the plasma erosion test, where the surfaces have been mirror polished before the test. It is clear that coatings prepared by conventional coarser powder (Y-c) have rougher eroded surfaces suggesting that large particles are generated and are easily deposited onto the Si wafer. On the other hand, use of fine powder (Y-5f and Y-1f) is found to be effective to retain smoother eroded surfaces in both dry feeding and slurry feeding. That suggests generation of smaller particles. As the RIE keeps evacuating using vacuum pump at etching process, small particles are easily exhausted from the chamber, which is effective to increase yield ratio of the Si devices by reduction of deposition onto the device. Smooth eroded surface is considered to generate smaller particles.

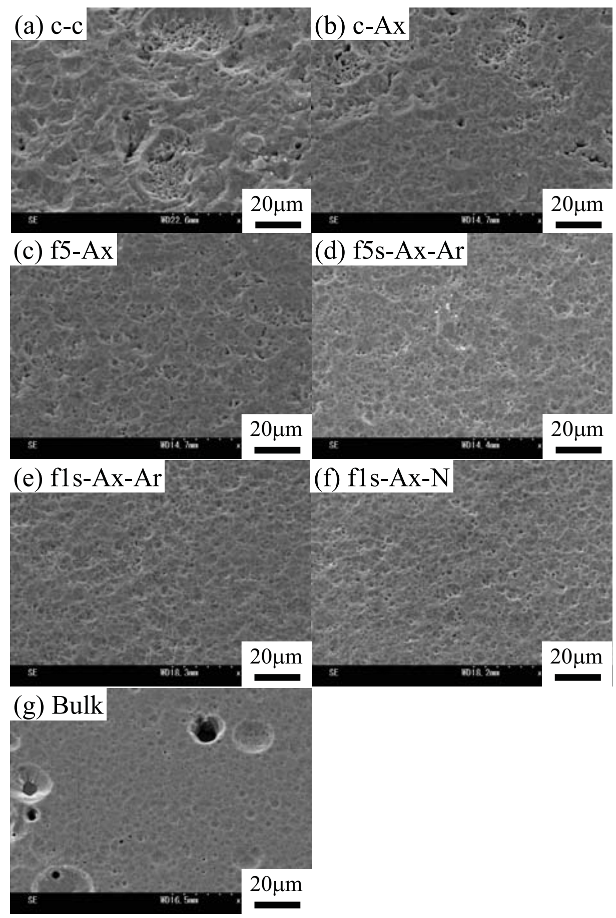


**Fig. 2.** SEM images of the specimens after the plasma erosion test.

Fig. 3 shows relation between plasma erosion rate and delta average surface roughness (ΔRa), which is estimated from Ra before and after the erosion tests. As the Ra before the erosion test (polished surface) is different among the specimens, in particular bulk has high Ra due to large sized pits, ΔRa has been selected to investigate the relation between plasma erosion rate and change in surface morphology. It seems the specimen with lower erosion rate results in lower ΔRa. Fine powder slurry technique is found to be quite effective to produce the coating with high erosion resistance as well as retention of smooth original polished surface. Among the coatings, the f1-Ax-N shows the best properties, where erosion resistance is 30% better than the conventional coating and roughness of eroded surface is almost comparable to bulk. Compared with the f1-Ax-Ar and f1-Ax-N, ΔRa is quite different meaning that plasma spray conditions strongly affect the coating properties.

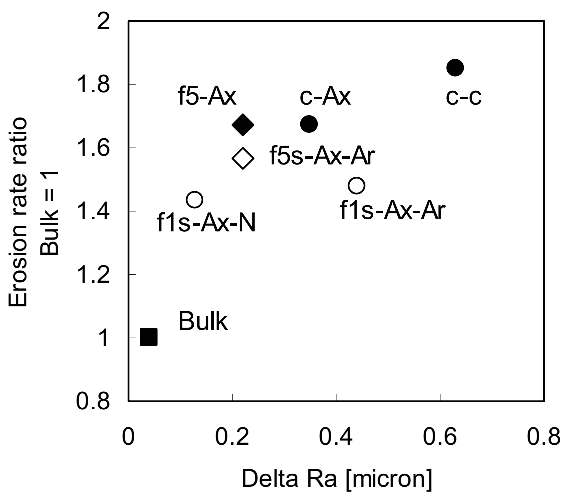


**Fig. 3.** Relation between plasma erosion rate and delta average surface roughness (ΔRa).

### 3.3 Micro Vickers hardness

Figure 4 shows micro Vickers hardness (HV) of the coatings and bulk as a reference. Twelve indentation tests were performed in each specimen and averaged HV values were obtained from ten tests by eliminating maximum and minimum values. Average HV are typically ranging from 350~450 when using conventional plasma spray equipment and conventional sized powders within our previous investigation. The result clearly shows that hard $Y_2O_3$ coatings of more than 600 HV have been successfully formed by high power plasma spraying of Axial III[tm] exept for f5-Ax.

Considering that high hardness of c-Ax than that of c-c and almost same porosity between these coatings, Axial III[tm] device is considered to have ability to increase binding strength between lamellae. However, hardness of the Axial III[tm] coatings is still lower to that of sintered bulk $Y_2O_3$ (700HV) in spite of quite lower porosity as for slurry coatings. This suggests room is remained to improve quality of Axial III[tm] coating by adjusting many parameters, such as powder size, powder dispersion in the slurry, slurry concentration, atomization of slurry, slurry feeding rate, plasma power, plasma gas composition, plasma gas feeding rate, stand off distance and so on.

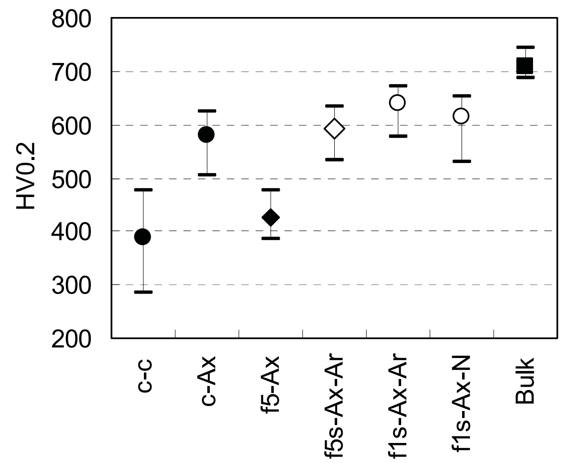


**Fig. 4.** Vickers hardness of the $Y_2O_3$ coatings and bulk.

### 3.4 Microstructure

SEM microphotographs of cross section of the coatings are shown in Fig. 5. Porosity by image analysis is also shown in the figures. The c-c coating in Fig. 5(a) was prepared after mirror polishing of the surface and the other coatings were prepared from as-sprayed specimens. It is clear that the slurry coatings have dense structure with few large-sized pores normally seen in the conventional spray coatings as shown in Figs. 5(a) and 5(b).

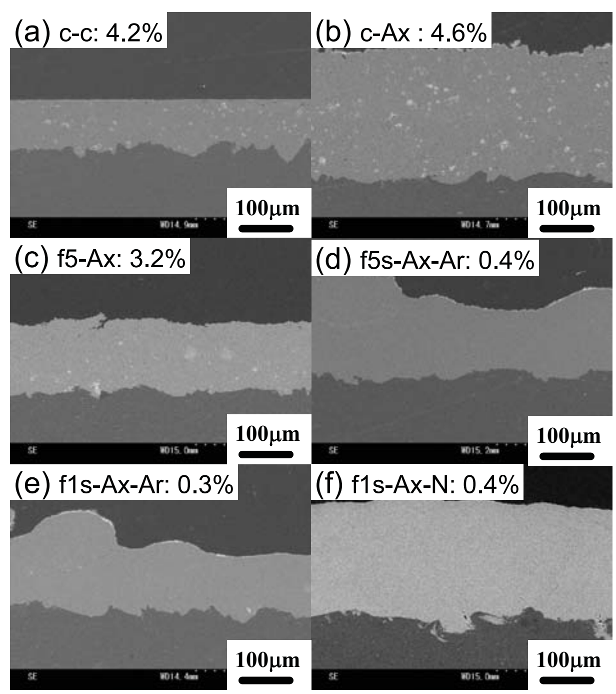


**Fig. 5.** Cross-sectional SEM micrographs of the coatings: (a) c-c, (b) c-Ax, (c) f5-Ax, (d) f5s-Ax-Ar, (e) f1s-Ax-Ar and (f) f1s-Ax-N.

Unclear microstructural difference is seen between Fig. 5(a) and 5(b) in spite of using different plasma gun where plasma power and powder injection direction are different.

Powder size seems to be dominant for coating density from comparison with Fig. 5(b) and 5(c). Slurry technique with fine powder is also effective for producing denser coating. Rugged surface morphologies are observed in the coatings of Fig. 5(d) and 5(e). Although its formation mechanism is unclear, atomization of slurry when injecting plasma plume may be important because a large sized droplet lead to a large splat. Fig. 5(f) shows smoother surface can be formed by adjusting slurry plasma spray conditions.

Magnified cross-sectional images by field emission SEM are shown in Fig. 6. In the c-c coating, lamellar structure is observed that is usually existing in the plasma spray coatings. Lamellar structure with smaller splats is also observed in the f5-Ax coating prepared using fine powder. On the other hand, microstructures of slurry coatings in Figs. 6(c) and 6(d) are apparently different from those of conventional plasma spray coatings. Only micro sized pores are seen in the slurry coatings and these imperfectness of the structure may result in lower hardness and lower plasma erosion resistance than sintered bulk.

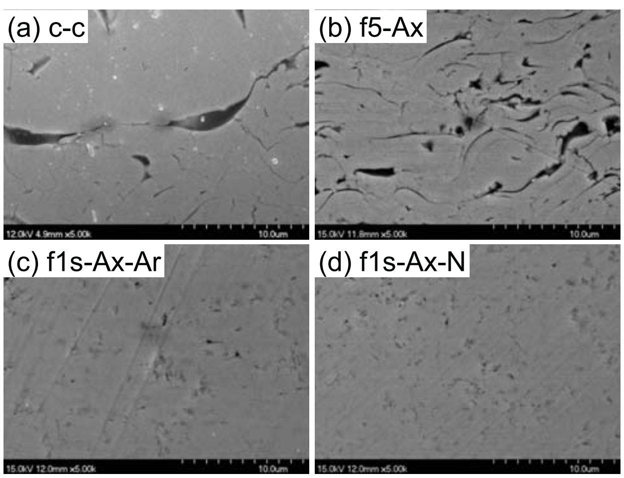


**Fig. 6.** Magnified Cross-sectional SEM micrographs of the coatings: (a) c-c, (b) f5-Ax, (c) f1s-Ax-Ar and (d) f1s-Ax-N.

### 3.5 Crystal structures

Crystal structures of the coatings are investigated by X-ray diffraction as shown in Fig. 7. Crystal structure of all feedstock powders of Y-c, Y-f5 and Y-f1 is only composed of cubic phase, which is well known as stable phase. As for the coatings from the Y-c powder (c-c and c-Ax), little change is observed for the crystal phase. When using smaller powder of Y-f5, although cubic phase is still major, another phase which is identified as meta stable phase of monoclinic phase, has appeared in the f5-Ax coating. The peak intensities of monoclinic phase becomes higher in the slurry coatings. Comparing with patterns for f5s-Ax-Ar and f1s-Ax-Ar, the f1s-Ax-Ar coating from smaller powder relatively contains high amount of monoclinic phase. Furthermore, cubic phase has almost disappeared in the f1s-Ax-N coating.

G.J. Vogt has reported formation of monoclinic phase of yttrium oxide [12]. In the reference, cubic phase of yttrium oxide powder of less than 45 μm has been introduced into radio frequency Ar-plasma (40 kW) chamber to vaporize or melt. Heated Ar gas with yttrium oxide has been quenched and the powders has been collected with separation (size classification) system. As a result, collected nano sized powder less than 100 nm mainly composed of monoclinic phase.

Considering that the previous work, it is considered that quenching process is necessary to make monoclinic phase of yttrium oxide, whose phenomenon might be similar to gamma phase formation of aluminum oxide in the plasma spraying. Use of finer powder (Y-1f) as well as of high enthalpy plasma (Nitrogen) is considered to be effective for increasing temperature of the powder qualitatively. The highly heated powder might contribute to formation of monoclinic phase effectively by intense quenching onto the substrates.

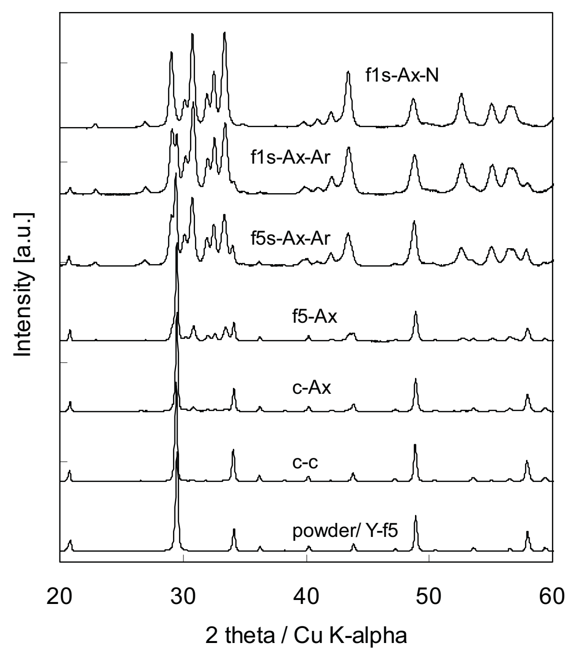


**Fig. 7.** X-ray diffraction patterns for powder (Y-5f) and the coatings.

## 4 Conclusions

Microstructures and crystal phase of the yttrium oxide ($Y_2O_3$) coatings prepared with high power axial injection plasma spraying using fine powder slurries have been studied in this paper, whose coatings have high density, high hardness and highly functional properties, such as highly plasma erosion resistance and retention smoother eroded surface. Although the properties of the best slurry coating is still inferior to bulk yttria, it is much better than that of the conventional plasma spray coatings. No lamellar microstructures have been seen from FE-SEM observation in the slurry coatings, which is quite different from the coatings with conventional feeding method. Meta stable phase of monoclinic phase has been formed when using finer powder of less than 5 μm. In particular, use of 1 μm with slurry system is effective for producing monoclinic phase that suggest intense quenching during spraying.

## 5 References


[1] Status and Perspective of Thermal Spray Markets 2004, Digital Research Institute Inc. (Nagoya, Japan), 2004 p. 20-33, in Japanese.

[2] Kobayashi, Y.: Current Status and Needs in the Future of Ceramics Used for Semiconductor Production Equipment, Proc. 37th Seminar on High-Temperature Ceramics, K. Matsuhiro, Ed., July 19, 2005 (Osaka, Japan), Japan Ceramics Society, 2005, pp. 1/7, in Japanese.

[3] Ohtsuki, H., Processing apparatus with a chamber having therein a high-corrosion-resistant sprayed film, Jpn. Pat. Appl. Publication, No. 2001-226773, Aug. 21, 2001.

[4] Kitamura, J., Mizuno, H., Kato, N. and Aoki, I.: Ceramic Coatings Prepared by Plasma Spraying for Semiconductor Production Equipments, Mater. Trans., 47, (2006), Issue 7, pp. 1677/83.

[5] Kitamura, J., Mizuno, H., Ibe, H. and Aoki, I.: Erosion Properties of Plasma Sprayed Ceramic Coatings Against Process Plasma in Semiconductor Production Equipment, Thermal Spray 2007: Global Coating Solutions, on CD-ROM, B.R. Marple, M.M. Hyland, Y.-C. Lau, C.-J. Li, R.S. Lima, and G.Montavon, Ed., May 14-16, 2007, (Beijing, China), ASM International, (2007), pp. 943/47.

[6] Kitamura, J., Ibe, H., Yuasa, F. and Mizuno, H.: Plasma Sprayed Coatings of High Purity Ceramics for Semiconductor and Flat-Panel-Display Production Equipment, J. Thermal Spray Technol., 17, (2008), Issue 5-6, pp. 495/501.

[7] Tang, Z., Yaroslavski, I., Hartell, P., Bogdanovic, N. and Burgess, A.: Axial Injection Plasma Spraying Using Micro and Nanopowder Slurries, Thermal Spray 2008: Crossing Borders, E. Lugscheider, Ed., June 2-4, 2008 (Maastricht, The Netherland), DVS, (2008), CD-ROM.

[8] Morishita, T., Osawa, S. and Itsukaichi, T.: HVOF Ceramic Coatings, Thermal Spray 2004: Advances in Technology and Application, ASM International, May 10-12, 2004, (Osaka, Japan), ASM International, (2004), CD-ROM.

[9] Berghaus, J. O., Bouaricha, S., Legoux, J.-G. and Moreau, C.: Suspension plasma spraying of nano-ceramics using an axial injection torch, Thermal Spray 2005: Explore its surfacing potential, E. Lugscheider, Ed., May 2-4, 2005 (Basel, Switzerland), DVS, (2005), CD-ROM.

[10] Waldbillig, D., Kesler, O., Tang, Z. and Burgess, A.: Suspension Plasma Spraying of Solid Oxide Fuel Cell Electrolytes, op. cit. ref. 4.

[11] Kitamura, J., Ibe, H., Yuasa, F., Tang, Z. and Burgess, A.: Structural, Mechanical and Erosion Properties of Plasma Sprayed Yttrium Oxide Coatings by Axial Injection of Fine Powder Slurries for Semiconductor and Flat-Panel-Display Applications, Thermal Spray 2009: Proc. International Thermal Spray Conf., B.R. Marple, M.M. Hyland, Y.-C. Lau, C.-J. Li, R.S. Lima, and G.Montavon, Ed., May 4-7, 2009, (Las Vegas, NV, USA), ASM International, (2009), pp. 567/572.

[12] Vogt, G.J.: Synthesis of the monoclinic yttria by thermal plasma processing, Proc. Electrochem. Soc. (1988), pp572/576.