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APPLICATION OF PLASMA DEPOSITION TECHNOLOGY FOR NUCLEAR FUEL FABRICATION

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ABSTRACT

Yttria-stabilized-zirconia (m.p. 2670°C), was deposited by induction plasma spraying system with a view to develop a new nuclear fuel fabrication technology. To fabricate the dense pellets, the spraying condition was optimized through the process parameters such as, chamber pressure, plasma plate power, powder spraying distance, sheath gas composition, probe position, particle size and its morphology. The results with a 5mm thick deposit on rectangular planar graphite substrates showed 97.11% theoretical density, when the sheath gas flow rate was Ar/H_2 120/20 L/min, probe position 8cm, particle size -75μm and spraying distance 22cm. The microstructure of YSZ deposit by ICP was lamellae and columnar perpendicular to the spraying direction. In the bottom part near the substrate, small equiaxed grains bounded in a layer. In the middle part, relatively regular size of columnar grains with excellent bonding each other were distinctive.

1. Introduction

Korea operates both PWRs and CANDUs. The synergy between the fuel cycles of PWR and CANDU reactors provides Korea with the potential merit of increasing the overall utilization of uranium and reducing the volume of spent fuel. On this basis, a fuel cycle concept, DUPIC(Direct Use of spent PWR fuel In CANDU reactors) has been in experimental study under international cooperation with Canada and the USA. The IAEA has also recently joined the program. The OREOX(Oxidation and Reduction of Oxide fuel) process was chosen to be the most promising option for DUPIC fuel fabrication, which does not involve any separation of sensitive materials and fission products[1-4]. Because of the high radiation fields emitted during fabrication of the pellets, all processes have to be performed in shielded facilities. It is therefore required that all fabrication processes should be simple. A lot of efforts are being devoted to the development of new technologies. Plasma spraying is a valuable technique for obtaining strong (30~40 MN/m^2) and dense (90~99%T.D.) films by spraying ceramic or metal powder on the surface of materials at high speed through a plasma jet [5]. Comparing to the other spraying methods, like flames, arcs and explosions, the plasma technique can generate ultra-high temperatures near 20,000

°K to serve as a heat source and is an amazing method to melt and spray high melting point materials such as tungsten, molybdenum and various ceramics. Up to now, this technique was usually applied to thin films having a thickness of a couple of μm to give some special properties to the surface of the material. Recently, this technology has been applied on the glassification of radioactive wastes. However, its application fields now extend to the production of high purity and high melting point material depositions, which are especially requisite for chemical reactions during spraying. In this study, the possibility of forming pellets with high density through the induction plasma spraying technique was evaluated as an alternative to the conventional multi-cycle oxidation/reduction and sintering processes, which are supposed to be a bottleneck for fuel fabrication. In addition, those parameters having an influence upon the deposition properties and the microstructure of the deposit were investigated.

2. Experimental System

2.1 Powder Material

As a surrogate for actual UO_2 powder, yttria-stabilized-zirconia(YSZ), including 20% Y_2O_3, was used. Two different morphology powders, METCO202NS (agglomerated, METCO Westbury, NY, USA) and AMDRY146 (sintered and crushed, Alloy Metal Co., Michigan, USA), were compared to investigate the effects on deposit density. The original particle size of METCO202NS and AMDRY146 were -150μm and -106+ 10μm, respectively, but these were divided into some groups to investigate particle size effects.

2.2 Equipment of Induction Plasma Spraying

100kW induction plasma equipment with a 300kHz r.f. plasma torch was used in this study. Ar gas was used as plasma gas, and H_2 or N_2 gas with Ar was used as sheath gas. Figure 1 is the spraying chamber with double walls with enforcing water for cooling, which is a 1.1m in diameter and 1.8m long and cylinder type. A CYLCO volumetric powder feeder (SYLVESTER company, Ohio, USA) with an 8 threads/inch driving screw was used. Ar gas was supplied as a carrier gas and the powder hopper was vibrated in order to feed the powder smoothly.

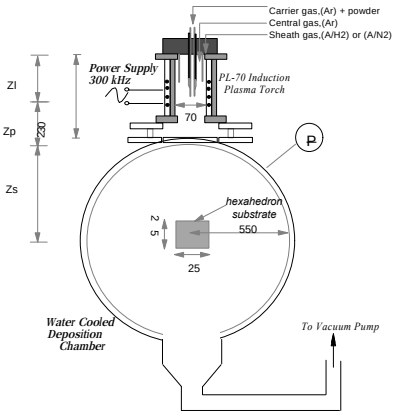

Fig. 1. Schematic drawing of the powder deposition chamber

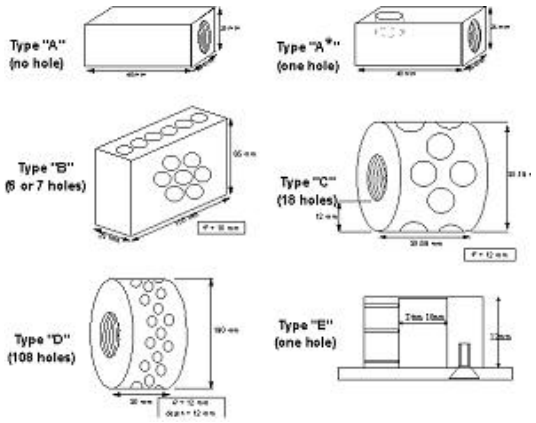

Fig. 2. Schematic of the different sample substrates

2.3 Molds for Pellet Formation

Figure 2 shows various kinds of specimen substrates or molds used in this study. Type 'A' mold, which is a rectangular type graphite bar, 25mm x 25mm x 40mm length, is generally used for optimizing the experimental parameters before forming the pellets. The other molds were also made with graphite and prepared for making real-sized pellets with 1 hole, 6 or 7 holes, 18 holes and 108 holes. The hole is the same size as a nuclear pellet of 10mm in diameter and 10mm in depth.

2.4 Fabrication of a Deposit

To fabricate the deposits, a rectangular graphite bar, 25mm × 25mm × 40mm, was used as a substrate. For thick deposit about 5mm thick, powder was sprayed for about 20 to 60 seconds. The specimens were cooled in an Ar atmosphere for 30 minutes. The specimens were then separated from the substrate and cut vertically by a diamond saw (Isomet 2000, Buehler). A cut section of the deposit was etched by a 50% hydrogen fluoride solution heated to its boiling point.

To get the samples of splats, powder was sprayed for a short time on a 2mm thick stainless steel plate fixed on a graphite substrate.

2.5 Analysis

A SEM (scanning electron microscope, Jeol JSM 840A, Japan Electron Optics Ltd., Tokyo) and a optical microscope (Letiz METALLUX 3, Iowa, USA) were used to study the microstructure of the deposit. Chemical composition of the spheroidized particles and deposits were measured by EPMA

(electron probe microscope analyzer, model SXR, CAMECA, Paris, France) with a beam size of 1 μm. The phases were analyzed by XRD (X-ray diffractometer, MXP3A-HF, Mac Science, Ishikawa, Japan) using $CuK\alpha_1$ radiation with graphite monochromator. The scanning angle was between 20 and 100° at intervals of 0.05° using a step counting time of 3sec. A TEM (transmission electron microscope, JEOL 2000 FX2, JEOL, Massachusetts, USA) was used to observe internal microstructure. Samples were prepared by mechanical thinning followed by ion milling. The density was evaluated by an image analyzer software, Mocha Image Analysis (Jandel Scientific), after taking some areas of the cut section of the deposit at 100 times magnification. The density was averaged from three randomly selected areas in the sample. The experimental design and analysis method, called ANOVA, was used to evaluate the effects of parameters [6].

3. Results and Discussions

3.1 Optimization of Spraying Conditions for METCO202NS by ANOVA Method

Table 1 shows the density variation of the deposits, sprayed YSZ202NS powder with combination of 4 parameters, chamber pressure (A), plate power (B), spraying distance (C), and the composition of the sheath gas (D) at the 2 levels. Effect 'I' identifies the standard condition for this series of runs. The effect 'a' means the pressure effect on the basis of condition 'I'. In the same way, 'b' means the plate power effect, and 'ab' means both the pressure and plate power effects on 'I' by changing them to other experimental conditions. Table 2 shows the results of the main and interaction effects and the F-value evaluated by ANOVA. 'A' denotes the relative effect of the parameter A, 'B' denotes the effect of the parameter B, and 'AB' denotes the combined effects of the parameters, A and B, together. According to the results of Table 2, the sensitive parameters on the deposit density were sheath gas composition, plate power, spraying distance and chamber pressure, in order.

This indicates that the plasma temperature is the most important factor for high density. The thermodynamic properties of plasma such as plasma mass density, internal energy, enthalpy, specific heat and entropy, relate to the plasma gas composition [7]. In this experiment, the effects of the plasma gas composition to the deposit density were investigated using Ar/H_2 (120/10 l/min) and Ar/N_2 (100/40 l/min). The results of ANOVA indicate that the plasma gas composition is a dominant parameter for the deposit density, meaning that the gas composition is more influential than other factors due to the thermodynamic properties.

Table 1. Design of the power deposition experiments of METCO202NS and its results

Effect	Treatment Combinations				Average
	A Pa (Torr)	B Pw (Kw)	C Zs (cm)	D Gx	Density (%)
I	200	80	30	Ar/H_2	88.58
a	400	80	30	Ar/H_2	83.69
b	200	60	30	Ar/H_2	79.38
ab	400	60	30	Ar/H_2	58.21
c	200	80	22	Ar/H_2	90.08
ac	400	80	22	Ar/H_2	88.29
bc	200	60	22	Ar/H_2	86.17
abc	400	60	22	Ar/H_2	80.65
d	200	80	30	Ar/N_2	73.64
ad	400	80	30	Ar/N_2	80.78
bd	200	60	30	Ar/N_2	63.47
abd	400	60	30	Ar/N_2	55.60
cd	200	80	22	Ar/N_2	71.34
acd	400	80	22	Ar/N_2	71.65
bcd	200	60	22	Ar/N_2	51.17
abcd	400	60	22	Ar/N_2	66.29

Table 2. ANOVA for power deposition experiments of METCO202NS

Source	Effect	Sum of Squares	Degree of freedom	Mean Squares	F value	Signi-ficance
A	2.333	65.310	1	65.310	8.431	0.007
B	13.389	2151.103	1	2151.103	277.692	0.000
AB	-2.526	76.583	1	76.583	9.886	0.004
C	-2.785	93.102	1	93.102	12.019	0.002
AC	4.363	228.420	1	228.420	29.487	0.000
BC	4.120	203.734	1	203.734	26.301	0.000
ABC	-5.296	336.603	1	336.603	43.453	0.000
D	15.244	2751.997	1	2751.997	355.263	0.000
AD	6.009	433.261	1	433.261	55.931	0.000
BD	-1.832	40.278	1	40.278	5.200	0.029
ABD	-2.475	73.532	1	73.532	9.493	0.004
CD	-6.046	438.685	1	438.685	56.631	0.000
ACD	0.324	1.258	1	1.258	0.162	0.690
BCD	1.665	33.250	1	33.250	4.292	0.046
ABCD	2.160	55.966	1	55.966	7.225	0.011
ERROR		247.884	32	7.746		
TOTAL		7230.968				

The density of the deposit is revealed to be not so much dependent on the chamber pressure as other factors. However, as shown in Table 1, the lower the chamber pressure, the higher the density was. The reason for the high density seems to the higher plasma temperature and the higher momentum of the particles at the lower chamber pressure. Of the factor interactions, both the combination of the spraying distance and sheath gas composition, source ‘CD’, and chamber pressure and sheath gas composition, source ‘AD’ were very influential factors to the density of the deposit. In this series of runs with YSZ METCO202NS, the highest density was 90.08% T.D. at the following conditions; chamber pressure 200Torr, plate power 80kW, sheath gas composition Ar/H_2(120/10 l/min) and powder spraying distance 22cm(the condition 'c' on Table 1).

3.2 Optimization of Spraying Conditions for AMDRY146 Powder

In order to optimize the spraying conditions with AMDRY146 powder, the effects of parameters such as, H_2 flow rate in a sheath gas of Ar/H_2, probe position in the torch, particle size and spraying distance were investigated. As shown in Table 3, the highest density was 97.11%T.D. at the following conditions; sheath gas of Ar/H_2 flow rate 120/20 l/min, probe position 8cm, particle size -75μm and spraying distance 22cm. According to the ANOVA conducted with two kinds of particle sizes, -75μm and -90μm, the deposit density was dependent on the particle size, powder spraying distance, and H_2 flow rate in the sheath gas in order, as shown in Table 4. In the case of two effect interactions, the

Table 3. Powder deposition experiments and results with -75 and -90μm AMDRY146

Effect	Treatment Combinations				Average Density (%)
	Sheath gas Ar/H_2, (slpm)	Zp (cm)	particle size, μm	Zs (cm)	
I	120/20	8	-75	30	95.51
a	120/10	8	-75	30	93.27
b	120/20	4	-75	30	94.49
ab	120/10	4	-75	30	89.76
c	120/20	8	-90	30	86.67
ac	120/10	8	-90	30	82.54
bc	120/20	4	-90	30	84.72
abc	120/10	4	-90	30	80.04
d	120/20	8	-75	22	97.11
ad	120/10	8	-75	22	94.64
bd	120/20	4	-75	22	96.60
abd	120/10	4	-75	22	94.25
cd	120/20	8	-90	22	94.80
acd	120/10	8	-90	22	89.15
bcd	120/20	4	-90	22	93.70
abcd	120/10	4	-90	22	87.50

Table 4. ANOVA for power deposition experiments of AMDRY146 -75 and -90μm

Source	Effect	Sum of Squares	Degree of freedom	Mean Squares	F value	Signi-ficance
A	4.054	197.235	1	197.235	39.531	0.000
B	1.579	29.925	1	29.925	5.998	0.020
AB	-0.433	2.253	1	2.253	0.452	0.506
C	7.063	598.688	1	598.688	119.993	0.000
AC	-1.111	14.807	1	14.807	2.968	0.095
BC	-0.221	0.585	1	0.585	0.117	0.734
ABC	-0.158	0.301	1	0.301	0.060	0.808
D	-5.092	311.203	1	311.203	62.373	0.000
AD	-0.112	0.150	1	0.150	0.030	0.864
BD	0.667	5.333	1	5.333	1.069	0.309
ABD	-0.326	1.274	1	1.274	0.255	0.617
CD	2.702	87.642	1	87.642	17.566	0.000
ACD	0.648	5.044	1	5.044	1.011	0.322
BCD	0.242	0.701	1	0.701	0.140	0.710
ABCD	-0.326	1.274	1	1.274	0.255	0.617
ERROR		159.660	32	4.989		
TOTAL		1416.076				

combination of particle size and powder spraying distance, source ‘CD’, was the most influential to the density of the deposit.

3.3 Forming a Surrogate Pellet for Development of Nuclear Fuel

Based on the results of spraying the METCO202NS powder and AMDRY146 powder on a fixed substrate, the pellet forming was conducted with pellet molds, shown in Figure 2 and 3. The density of the pellet in the revolving mold was only 94% of T.D. This seems to be an unexpected factor that the direction of the molten particle was not coincident to the longitudinal direction of the hole of the mold while spraying. However the shape of the pellet was excellent as shown in Figure 4.

Fig. 3. Induction plasma spraying of YSZ powder on Type "D" mold

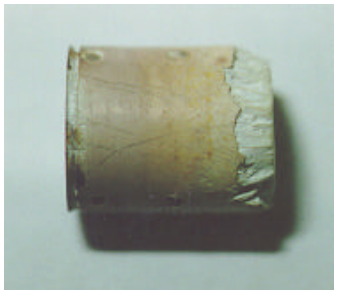

Fig. 4. Pellet of YSZ of 10mm Dia. X 10mm H.

3.4 Microstructure of the Deposit

The microstructure about 5mm thick deposit was lamellae and columnar structure perpendicular to the spraying direction. In the bottom part near the substrate, equiaxed and columnar grains bounded in a layer, a ' brick wall' named by Sampath and Herman [8], pores and cracks were observed. In the middle part, relatively regular sized columnar grains, about 100μm thick and 300μm long, through many layers with excellent bonding and dense microstructure were distinctive. In the upper part, the microstructure was the same as the middle, but the sizes of columnar grains were irregular.

The shape of the layer depends on the ability to adhere by impact and deformation on the substrate or previously solidified splats [9]. However, the bottom layer contact to the graphite substrate generally were fine-grained equiaxed and in partly columnar grains separated by a horizontal gap due to poor contact between layers, and vertical cracks as shown in Figure 5. In the middle part of the deposit, no boundary lines between layers were observed. The grains were grown through the layers. Figure 6 shows the long columnar grains developed in the middle part of the deposit. Grains were thicker and longer than the other parts, and some of the grains reached 100 μm thick and 300 μm long.

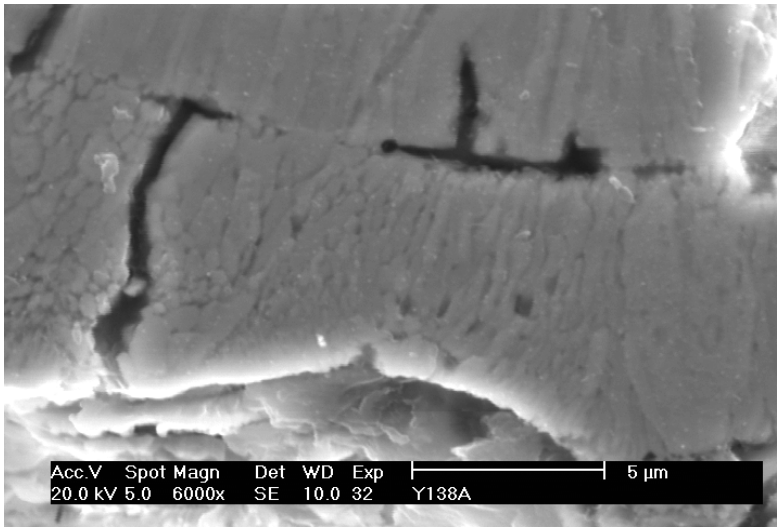

Fig. 5. Microstructure of YSZ splats solidificated on the surface of the graphite substrate (Deposition condition: particle size -75㎛, Ar/H2=120/20 L/min, chamber pressure 200 Torr, Zp=8cm, Zs=22 cm).

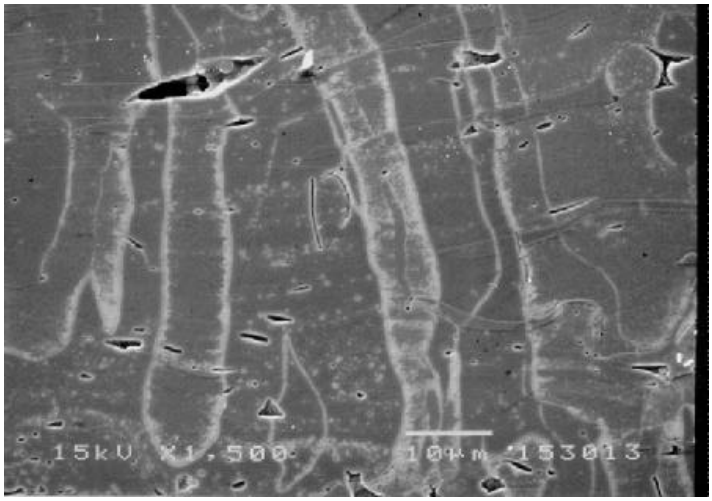

Fig. 6. Columnar gains developed in the middle part of the deposit (Deposition condition: particle size -75㎛, Ar/H_2=120/20 L/min, chamber pressure 200 Torr, Z_p=8cm, Z_s=22 cm).

4. Conclusion

Thick deposit with the METCO202NS powder, both the plasma gas composition and plate power were found to be the most influential factors on the density. This means that the plasma temperature is an important factor for high melting point ceramics. In the case of two parameter interactions, the combination of sheath gas composition and powder spraying distances greatly affect on the density. In the optimization with AMDRY146 in various process parameters, such as sheath gas composition, probe position, particle size and spraying distance, the highest density was 97.11 % T.D. at the following parameters; sheath gas flow rate 120/20 l/min, powder spraying probe position 8cm, particle size -75μm and spraying distance 22cm. Comparing this to the results of METCON202NS, the powder property and particle size were found to be very important on the density.

The microstructure of the bottom part of the deposit showed equiaxed small grains. Equiaxed small grains were prevailed when the droplets were quenched rapidly on the substrate, this may be a large *DT* due to the rapid quenching. In the middle part of the deposit, large columnar grains, about 100 ㎛ thick and 300 ㎛ long, were developed through the layers with strong adhesion between layers.

From the optimum condition attained with a fixed substrate, pellets with a nice exterior view and a density of 94% T.D. were formed.

Although real fuel materials were not used in these experiments, it is very meaningful to apply a plasma technique to nuclear fuel fabrication field. By fine-tuning the spraying conditions and with additional devices, it would be possible to form high density pellets near 96% T.D. as is required for nuclear fuel. For an application to a real nuclear fuel, other required properties such as, thermal conductivity, mechanical strength, etc. have to be investigated. The technique for controlling the grain size during processing should be further investigated.

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