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Synthesis of zirconia sphere particles based on gelation of sodium alginate

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Abstract

Zirconia sphere particles were synthesized through the gelation process of Na-alginate, and cermet (ZrO_2-Mo) pellets were fabricated under several conditions. In this process, a zirconia slurry was prepared by mixing oxide powders (ZrO_2, Y_2O_3, Er_2O_3, CeO_2), distilled water and Na-alginate, and subsequently dropped into $CaCl_2$ solution. As a result, zirconia sphere particles coated with a gelled film were synthesized. The slurry density (zirconia content in slurry) of 30-64 wt% and Na-alginate concentration of a few % were good for gelation for up to 10 wt% $CaCl_2$ solution. Sphere particles with smaller diameter were obtained by dropping slurry with a mechanical vibration. The prolongation of the ball milling time for mixture of oxide powders was effective to increase the sintered density of zirconia sphere particles, especially for higher CeO_2 concentration. The dense cermet pellets were fabricated for max. 50% volume ratio of zirconia phase for Mo matrix using zirconia particles covered with Mo powder by a rotating granulation method.

Keywords: zirconia, inert matrix fuel, gelation, sodium alginate, cermet

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1. Introduction

Zirconia-based oxide fuel, which is so-called “inert matrix fuel (IMF)”, is an attractive one to burn excess plutonium and minor actinides (MAs) which are generated from reprocess of spent fuels and from dismantlement of nuclear weapons [1]. Because, it has some advantages such as a high melting point, a low neutron capture cross-section, a stability against irradiation for utilization as a nuclear fuel. In addition, its leachability in the geological repository is still lower than that of glass due to the chemical stability [2], which also means its nuclear proliferation resistance. Therefore, the zirconia-based oxide fuel has been developed to suit the once-through fuel cycle and is also one of candidates of the host material of a deep-burn fuel in a novel concept of nuclear fuel cycle [1].

As is well known, cubic zirconia essentially has the lower thermal conductivity since it involves oxygen vacancies in the lattice. For instance, the thermal conductivity of cubic stabilized zirconia is approx. 2-3 $W \cdot m^{-1}K^{-1}$ [3]. Hence, to improve the thermal performance, zirconia doped with actinides is anticipated to be used as a composite fuel, i.e., cermet (ceramic-metal) or cercer (ceramic-ceramic). In previous studies, several types of such composite fuels were assessed, e.g., homogeneous or heterogeneous mixing of matrix and dispersive phases [1,4]. So far, we have developed the internal gelation method to synthesize zirconia sphere particles as a dispersive phase of a heterogeneous type fuel [5,6]. However, a large amount of waste solution, e.g. silicone oil, kerosene and ammonium solution, was generated through this method. Therefore, we aimed to develop the simple synthesis method with a low environmental impact, which is based on the gelation process of sodium alginate [7-9]. Na-alginate is known as a natural organic material and widely used in the food industries. Major parts of waste through this method are, therefore, $CaCl_2$ solution and water. Furthermore, most of processes of this method are carried out at room temperature except the sintering process.

In this study, we systematically assessed the processes of the synthesis method based on Na-alginate gelation reaction to form zirconia sphere particles. Furthermore, manufacturing processes of Mo matrix cermet were discussed.

2. Experimental

2.1. Synthesis of zirconia sphere particles via Na-alginate gelation reaction

Before the synthesis of sphere particles of multi-component zirconia (ZrO_2-Y_2O_3-Er_2O_3-CeO_2), using only yttria-stabilized zirconia (Tosoh, TZ-8Y) powder, several suitable conditions were assessed for gelation of the zirconia slurry, e.g. an amount of zirconia in slurry, Na-alginate concentration, $CaCl_2$ concentration. Processes of the synthesis of gel spheres of yttria-stabilized zirconia were same as those of multi-component zirconia.

The flowchart of synthesis of zirconia sphere particles is shown in Fig. 1 (a). Firstly, raw oxide powders of ZrO_2 (Tosoh, TZ-0), Y_2O_3 (Kanto), Er_2O_3 (Kojundo) and CeO_2 (Kanto) were mixed in a ball mill while Na-alginate (Kanto) solution was prepared. Here, Y_2O_3 was added into zirconia as a stabilizer to maintain a fluorite lattice structure, Er_2O_3 was a burnable poison, CeO_2 was a surrogate for PuO_2 or MA oxides. Secondary, mixed zirconia powder and Na-alginate solution was mixed well to prepare the zirconia slurry. Thirdly, the zirconia slurry was dropped into $CaCl_2$ (Kanto) solution to cause the gelation reaction in which Na^+ exchanged for Ca^{2+}. This ion exchange reaction is naively given as follows:

$$Ca^{2+} + 2(C_6H_7O_6\text{-}Na) \rightarrow 2Na^{+} + (C_6H_7O_6\text{-}Ca\text{-}C_6H_7O_6) \qquad (1)$$

As a result, small slurry droplets covered with a thin gelled film (Ca-alginate) formed in $CaCl_2$ solution. In this study, two methods were tested for dropping slurry. One was that zirconia slurry was dropped with a dispensing burette by hand and the other is that the slurry was slowly pushed by a syringe pump and shaken by a vibration motor attached to a syringe. Fourthly, gel spheres were washed with distilled water, and subsequently dried at 373 K for 2 h in a thermostatic oven to reduce the drying time. Finally, dried sphere particles thus obtained were sintered at 1873 K for 8 h in air.

2.2. Fabrication of Mo matrix cermet

Mo matrix cermet was fabricated according to the flowchart shown in Fig. 1 (b). Firstly, Mo powder (Kojundo, purity: 99.99%, particle size: ca.2-3 μm) and zirconia sphere particles were mixed. Two mixing methods were tested. One was mixing with a spatula in an agate mortar and the other was using a rotating granulator. Here, as zirconia sphere particles, either dried particles or sintered ones were used. Secondary, a mixture of Mo powder and zirconia particles was formed into a pellet by uniaxial pressing at 200 MPa. Finally, the pellet was sintered at 1873 K for 8 h in Ar-5%H_2 flowing gas.

2.3.Characteriztion of zirconia sphere particles and cermet

Thermogravimetry (TG) and differential thermal analysis (DTA) were performed to investigate the behavior of zirconia spheres in heating. Measurements were done under the condition of heating rate = 5 $K \cdot min^{-1}$ in flowing dried air by a thermal analysis system (Seiko, SSC5200).

The lattice structure of sintered zirconia particles was evaluated by X-ray diffraction (XRD) measurement. The diffraction patterns were acquired using an X-ray diffractometer with Cu-Kα radiation (Rigaku, Multi-Flex). The measured diffraction angle 2θ was varied from 20º and 100º.

The microstructures of sintered sphere particles and cermet were observed by a scanning electron microscope (Shimadzu, SS-550). Surfaces of the observed sections were mechanically polished on abrasive papers and then subsequently finished by alumina buffing. Then the surface of the examined section was covered with Pt thin film. Furthermore, in order to evaluated the compatibility between Mo matrix and zirconia phase, elemental analyses were performed by an energy dispersive X-ray spectroscopy (EDAX, Genesis2000) attached to the SEM.

3. Results and discussion

3.1. Synthesis of zirconia gel sphere particles and their thermal property

Suitable conditions for preparation of gel sphere particles were assessed using yttria-stabilized zirconia powder. The results are summarized in Table 1. To easily handle zirconia slurry, especially for dropping, zirconia slurry should have a certain degree of fluidity. However, for lower concentration of zirconia in slurry (< 30 wt%), the lower sintered density was obtained. In contrast, for higher zirconia concentration (> 64 wt%), its slurry had a high viscosity, and consequently was hard to drop into $CaCl_2$ solution. Therefore, the slurry with 30-64 wt% zirconia content was suitable for such processes. In order to form the "sphere" particle, an amount of Na-alginate in slurry was controlled. For lower Na-alginate concentration (< 1 wt%), gel particles were too fragile to handle for the following process, e.g. washing, and were ellipsoidal rather than spherical. On the other hand, zirconia slurry with high Na-alginate concentration (> 2 wt%) was solidified before dropping. As a result, 1-2 wt% Na-alginate concentration is good to form solid gel spheres. To cause a gelation, a proper amount of Ca which exchanged for Na was needed in $CaCl_2$ solution. In the range of 1-10 wt% $CaCl_2$ concentration, the slurry smoothly underwent the gelation reaction in $CaCl_2$ solution. From the point of view of contamination, the low concentration of $CaCl_2$ should be favorable. We therefore used 40 wt% zirconia slurry, 1 wt% Na-alginate solution and 3 wt% $CaCl_2$ solution as a standard condition in this study.

TG and DTA curves of zirconia sphere particles via the Na-alginate gelation process showed an endothermic peak originated from vaporization of water around 400 K. Other peaks are so small and unclear. Hence, zirconia sphere particles formed via this process smoothly crystallize rather than gel spheres synthesized via other wet routes, e.g. the internal gelation [5,6]. Because, compared with contamination in gel spheres synthesized via the internal gelation, e.g. unreacted organic materials and byproducts, most of contamination from the gelation process of Na-alginate is water.

3.2. Relationship between sintering behavior of zirconia sphere particles and manufacturing process

For sintering of a solid solution of multi-component zirconia, homogeneously mixing of raw powders was needed. For instance, inhomogeneously mixing of MOX powders (UO_2 and PuO_2) causes gathering Pu elements ("Pu spot") in MOX fuels. In this study, multi-component oxide powders were, therefore, mixed in a ball mill. Those raw oxide powders and ethanol were cast into an alumina pod together with zirconia balls (ϕ5 and ϕ10) for mixing and grinding. The relationship between a degree of sintering and the milling time is shown in Fig. 2 for two kinds of zirconia (Zr:Y:Er:Ce = 75:10:5:10, 65:10:5:20 in mol%). For both cases, zirconia content was 40 wt% in slurry. For an image analysis in this study, the pore occupancy was defined as the ratio of area occupied by pores to total area of oxide sample observed by the SEM. Although the pore occupancy differs from so-called sintering density, it of course strongly reflects a degree of sintering. In this figure, zirconia sinters better as a decrease of Ce concentration and as an increase of the milling time.

Two methods for dropping zirconia slurry were tested, which were dropping with a burette by hand and with a mechanical vibration (syringe pump plus vibration motor). For both cases, the chemical composition of zirconia was Zr:Y:Er:Ce = 75:10:5:10. Difference in diameter of sintered particles between them is shown in Fig. 3. The former method results in Fig. 3 (a) and the latter method results in Fig. 3 (b), respectively. Sintered sphere particles had smaller diameters by the mechanical vibration method, and the effect was found to be still larger for 40 wt% zirconia slurry than for 50 wt% one.

3.3.Lattice structure of sintered zirconia particles synthesized via Na-alginate gelation

X-ray diffraction patterns in Figs. 4 (a) and (b) were measured for as-sintered zirconia particles with chemical compositions of Zr:Y:Er:Ce = 75:10:5:10 and 65:10:5:20, respectively. It is clearly shown that sintered sphere particles in this study have a fluorite lattice structure. The lattice constants determined for the fluorite structure are compared with those of zirconia particles obtained via the internal gelation method in Fig. 5 [6,10,11]. In addition, the values calculated by the semi-empirical equation are plotted [12]. As shown in this figure, the consistent results are obtained among different synthesis methods less than or equal to 35 mol% of additive elements. This means that zirconia solid solution forms in each sintered particles.

3.4. SEM examination of cermets

Mo matrix cermets were observed by a SEM and a stereomicroscope with a digital camera. In this study, Mo powder and zirconia particles were mixed by two different methods as already mentioned. For cermets in Fig. 6, Mo powder and zirconia particles were mixed with a spatula in an agate mortar. On the other hand, for cermets in Fig. 7, they were mixed in a rotating granulator. Furthermore, for zirconia particles in images of (a) and (c) in each figure, dried zirconia particles were used, and for those in images of (b) and (d), once sintered ones were used. All cermets in Figs. 6 and 7 have the 30 % volume ratio of oxide phase to Mo matrix. As shown in Fig. 6, compared with cermet in the image (a), that in the image (b) has some large cracks. This resulted from the difference in the degree of shrinkage between Mo matrix and zirconia particle during heating. Once sintered zirconia particles shrank little in the sintering process of cermet. In Fig. 6 (c), some cracks can be found in each zirconia particle. As the sintering of dried particles proceeded, those zirconia particles were strongly compressed by sintering of Mo matrix, which caused the generation of those cracks. In Fig. 6 (d), some cracks were found in zirconia particles, and large void was also observed between Mo matrix and a zirconia particle. This would be the reason that Mo powder and once sintered particles did not fully mix by this method. Furthermore, as a result, some sintered particles directly connected with each other, and these cracked in the process of pressing or sintering. On the other hand, Figs. 7 (a) and (c) show almost the same result as Figs. 6 (a) and (c), too. Therefore, the rotating granulator was little effective for using dried zirconia particles. However, as shown in Figs. 7 (b) and (d), this method was surprisingly effective for using once sintered zirconia particles. There was found few cracks in the cermet pellet and zirconia particles, and Mo matrix relatively well sintered. In addition, the mixing method using a rotating granulator is also effective for the cermet with the oxide phase volume ratio of 50%. This would result from that sintered zirconia particles were coated with Mo powder in the rotating granulator before pelletization.

Regardless of homogeneous or heterogeneous cermet, such composite fuels should have a compatibility between matrix and dispersive phases since the structural strength or other material properties could degrade due to a chemical reaction between them in high temperatures. The results obtained from EDX analyses for cermet, which was sintered using dried zirconia particles, are shown in Fig. 8. Element distributions of Mo as matrix phase and Zr, Ce as constituents of a zirconia particle were analyzed around an interface between Mo matrix and a zirconia particle. Y and Er distributions showed a same trend as Zr and Ce ones. From these images, we can clearly observe a boundary between Mo and zirconia phases, which means that the compatibility between them maintained during heating.

4. Conclusions

In this study, zirconia sphere particles were successfully synthesized via the Na-alginate gelation reaction. The suitable conditions to form sphere particles are: (1) zirconia content in slurry is 30-64 wt%; (2) Na-alginate concentration is a few % in slurry; (3) $CaCl_2$ concentration of 3 wt% in solution is enough for gelation. To obtain sphere particles with smaller diameter (~0.3 mm), the mechanical vibration method is effective. For higher concentration of CeO_2 in zirconia, the sintered density of sphere particles increased due to the prolongation of the ball milling time for mixing and grinding of raw oxide powders.

Manufacturing processes were also assessed for Mo matrix cermet with oxide phase of max. 50 vol%. For sintering cermet, to use dried zirconia particles as oxide dispersive phase reduced large cracks in a pellet but some cracks in oxide particles were found. On the other hand, once sintered particles readily generated cracks in the pellet. For both cases, these cracks formed due to the difference in a shrinkage rate between metal matrix and oxide phases during heating. This study also showed that coating sphere particles with Mo powder in a rotating granulator reduced these cracks. In addition, Mo matrix cermet showed a good compatibility between Mo and zirconia phases.

Acknowledgments

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Figure captions

Fig. 1. Flowcharts of (a) synthesis of zirconia sphere particles via Na-alginate gelation and (b) fabrication of Mo matrix cermet.

Fig. 2. Relationship between sintering property and ball milling time. Pore occupancy was defined as the ratio of occupied area by pores to total area of oxide particle observed by SEM.

Fig. 3. Diameter distributions of sintered sphere particles which underwent dropping with a burette by hand (a) or with a mechanical vibration (b).

Fig. 4. X-ray diffraction patterns obtained from sintered zirconia particles with chemical compositions of (a) Zr:Y:Er:Ce = 75:10:5:10 and (b) 65:10:5:20 in mol%.

Fig. 5. Lattice constants of sintered zirconia particles synthesized by several experiments as a function of an amount of additive ions, together with semi-empirical values.

Fig. 6. Photographs and SEM images of cermet pellets. Mo powder and zirconia particles were mixed with a spatula in an agate mortar, and dried particles and once sintered particles were used for sintering cermets in (a,c) and (b,d), respectively.

Fig. 7. Photographs and SEM images of cermet pellets. Mo powder and zirconia particles were mixed in a rotating granulator, and dried particles and once sintered particles were used for sintering cermets in (a,c) and (b,d), respectively.

Fig. 8. EDX analyses around a boundary between Mo and zirconia phases in cermet. Observed sample was same as one in Fig. 7 (a,c).

Table 1. Assessment of conditions for preparation of gel sphere particles via Na-alginate gelation

Parameter	Condition	Remarks
Zirconia content in slurry	< 30 wt%	Low sintered density
	30-64 wt%	Suitable
	> 64 wt%	Highly-viscous to drop
Na-alginate concentration in slurry	< 1 wt%	Fragile and non-spherical gel particle
	1-2 wt%	Suitable
	> 2 wt%	Solidified in preparing slurry
$CaCl_2$ concentration in solution	1-10 wt%	Successful

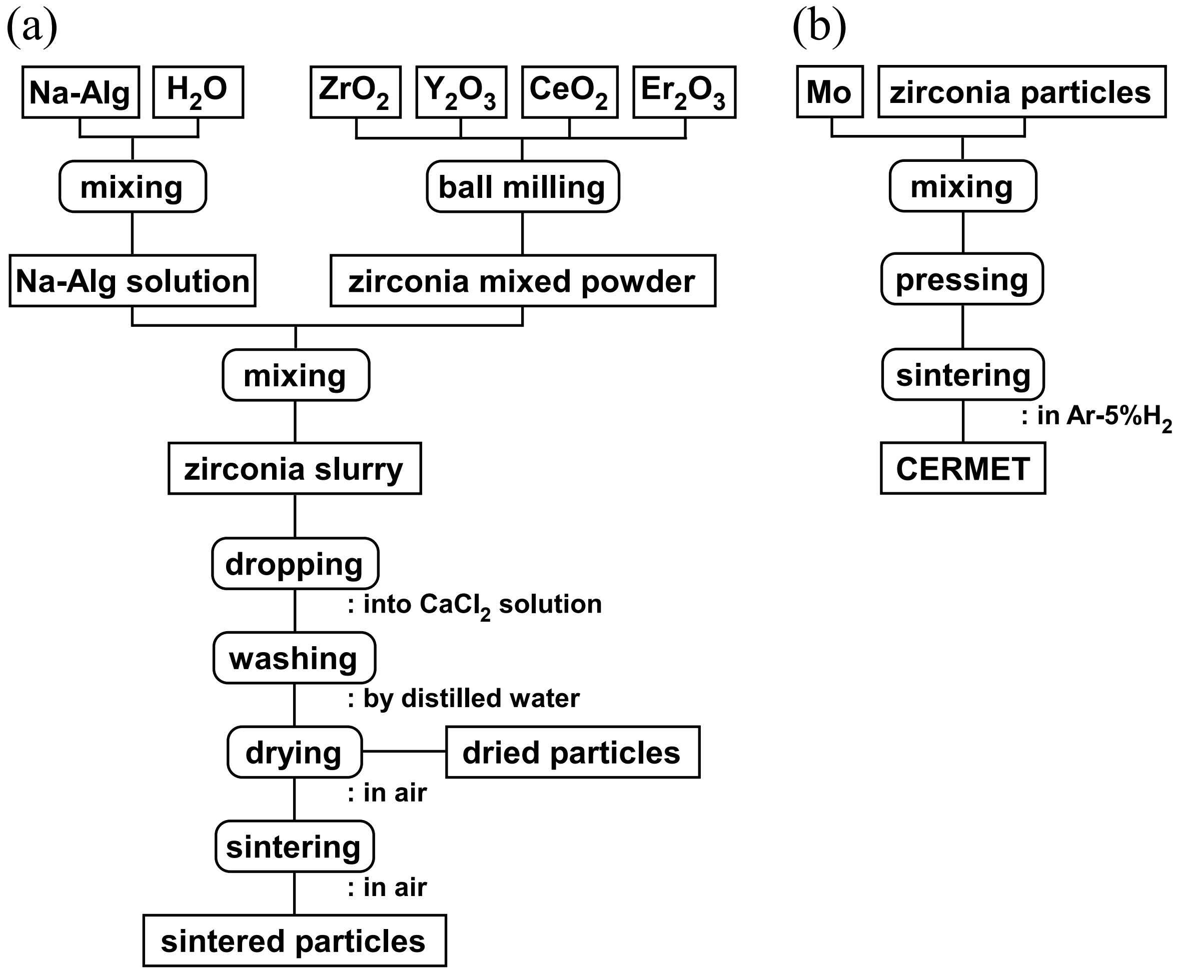
(a)
Na-Alg
H_2O
ZrO_2
Y_2O_3
CeO_2
Er_2O_3
mixing
ball milling
Na-Alg solution
zirconia mixed powder
mixing
zirconia slurry
dropping
: into $CaCl_2$ solution
washing
: by distilled water
drying
dried particles
: in air
sintering
: in air
sintered particles
(b)
Mo
zirconia particles
mixing
pressing
sintering
: in Ar-5%H_2
CERMET

Fig. 1

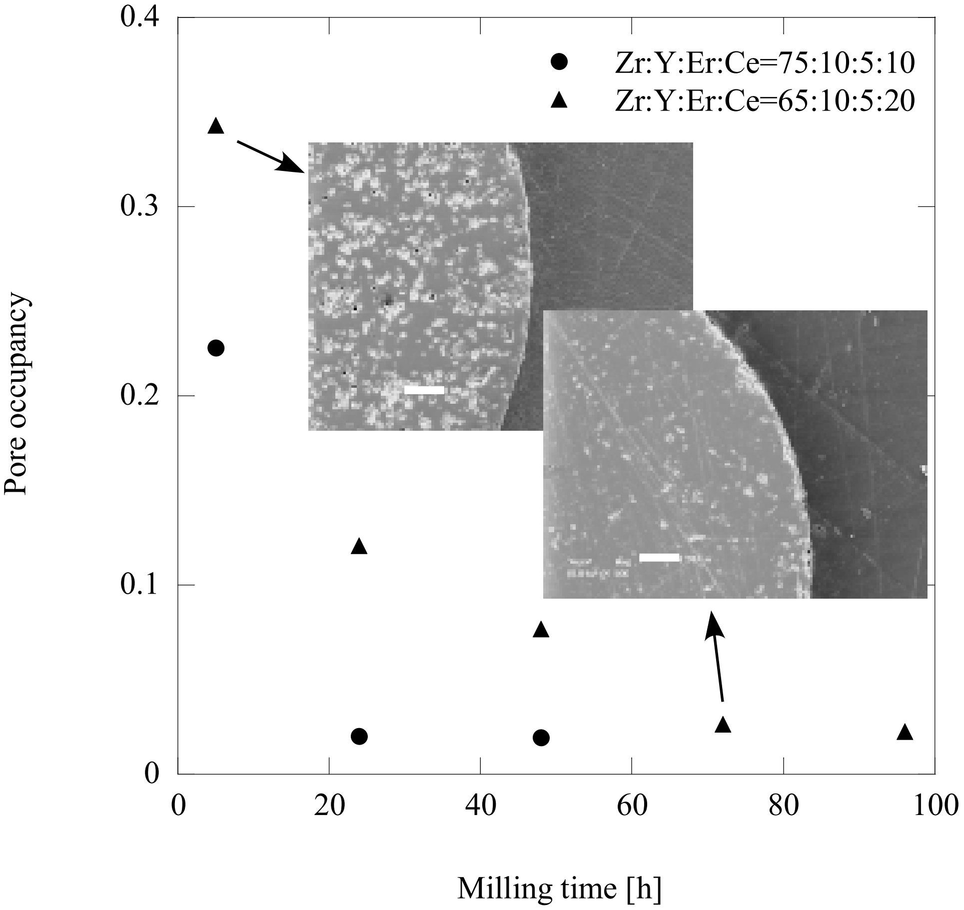
0.4
0.3
0.2
0.1
0
Pore occupancy
0
20
40
60
80
100
Milling time [h]
● Zr:Y:Er:Ce=75:10:5:10
▲ Zr:Y:Er:Ce=65:10:5:20

Fig. 2

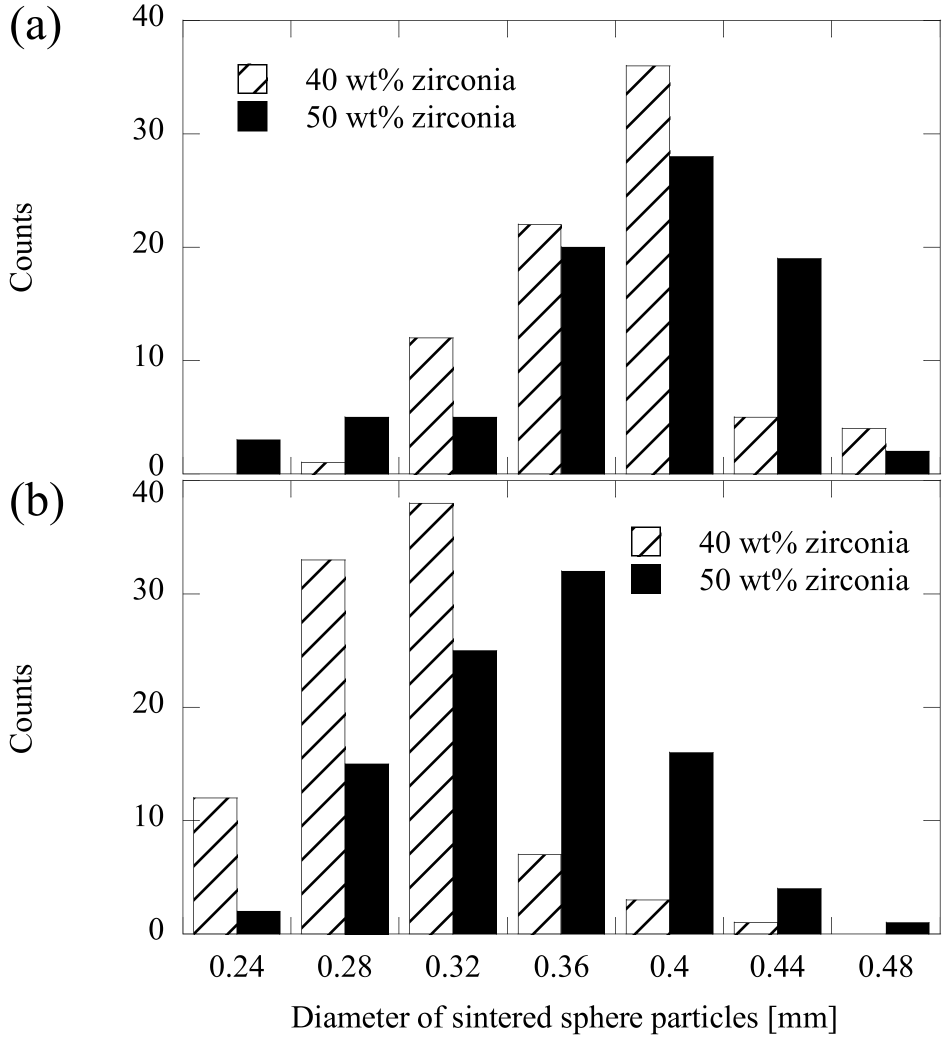
(a)
40
30
20
10
0
Counts
▨ 40 wt% zirconia
■ 50 wt% zirconia
(b)
40
30
20
10
0
Counts
▨ 40 wt% zirconia
■ 50 wt% zirconia
0.24
0.28
0.32
0.36
0.4
0.44
0.48
Diameter of sintered sphere particles [mm]

Fig. 3

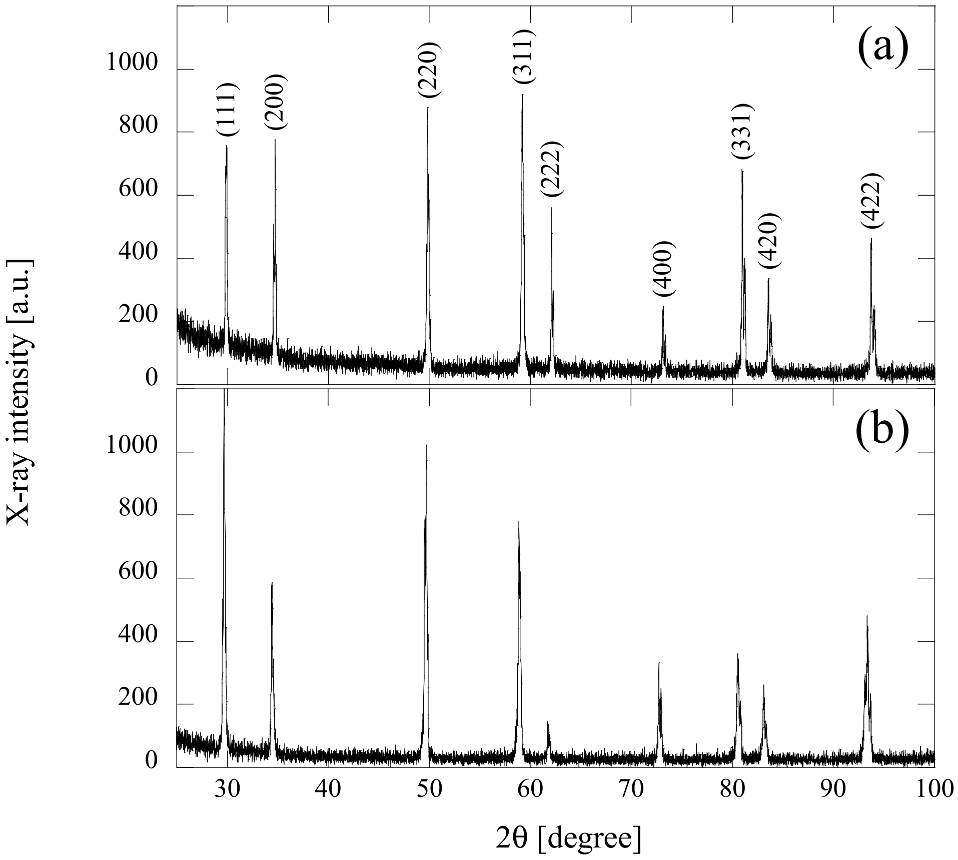
(a)
(b)
(111)
(200)
(220)
(311)
(222)
(400)
(331)
(420)
(422)
X-ray intensity [a.u.]
0
200
400
600
800
1000
30
40
50
60
70
80
90
100
2θ [degree]

Fig. 4

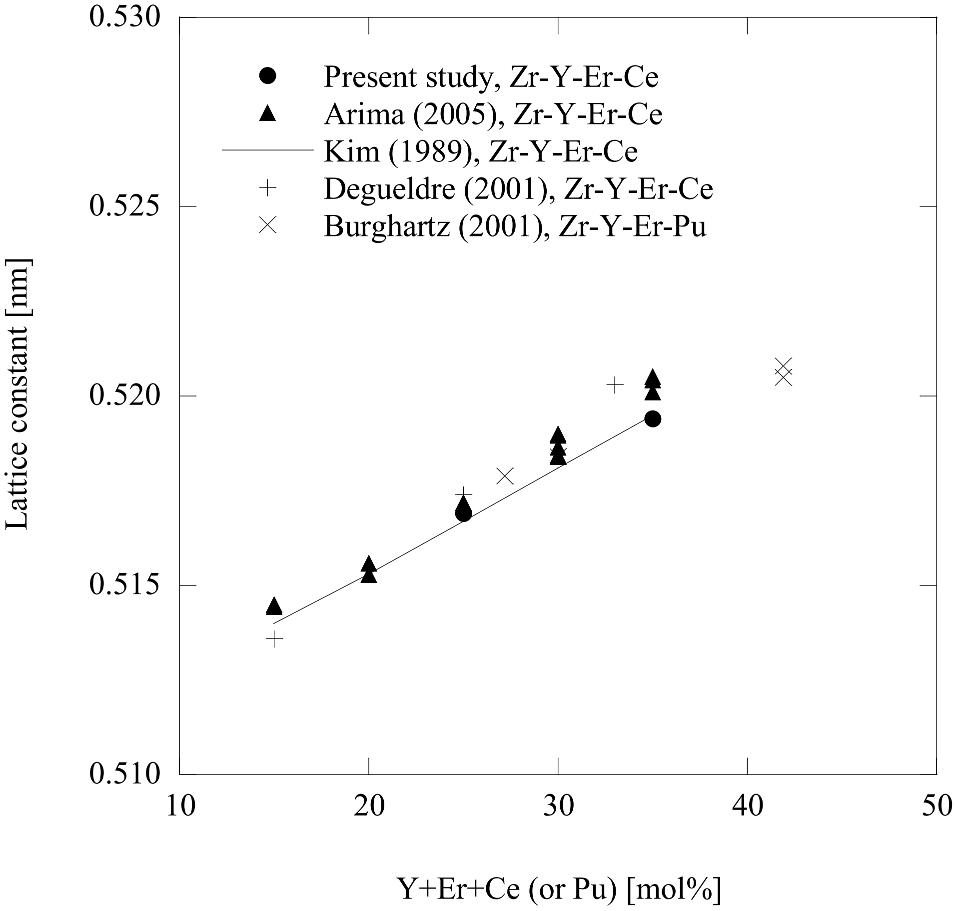
0.530
0.525
0.520
0.515
0.510
10
20
30
40
50
Lattice constant [nm]
Y+Er+Ce (or Pu) [mol%]
● Present study, Zr-Y-Er-Ce
▲ Arima (2005), Zr-Y-Er-Ce
Kim (1989), Zr-Y-Er-Ce
+ Degueldre (2001), Zr-Y-Er-Ce
× Burghartz (2001), Zr-Y-Er-Pu

Fig. 5

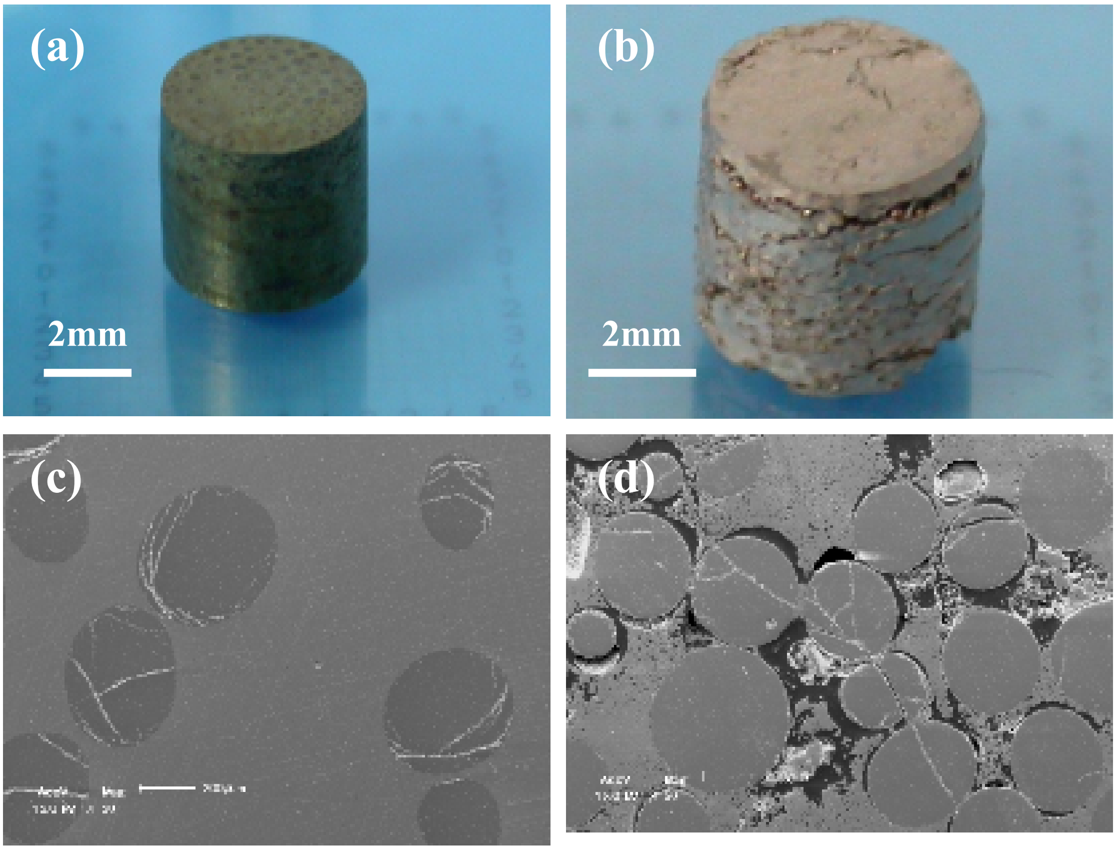

Fig. 6

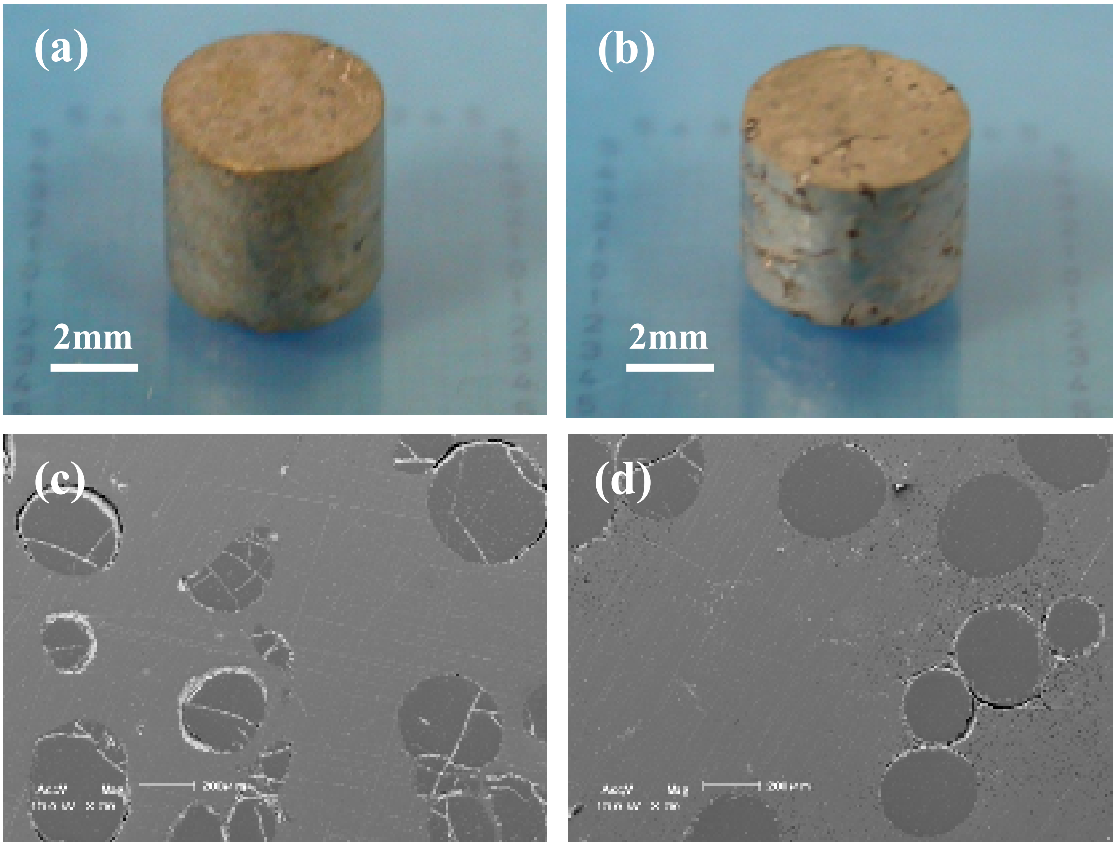

Fig. 7

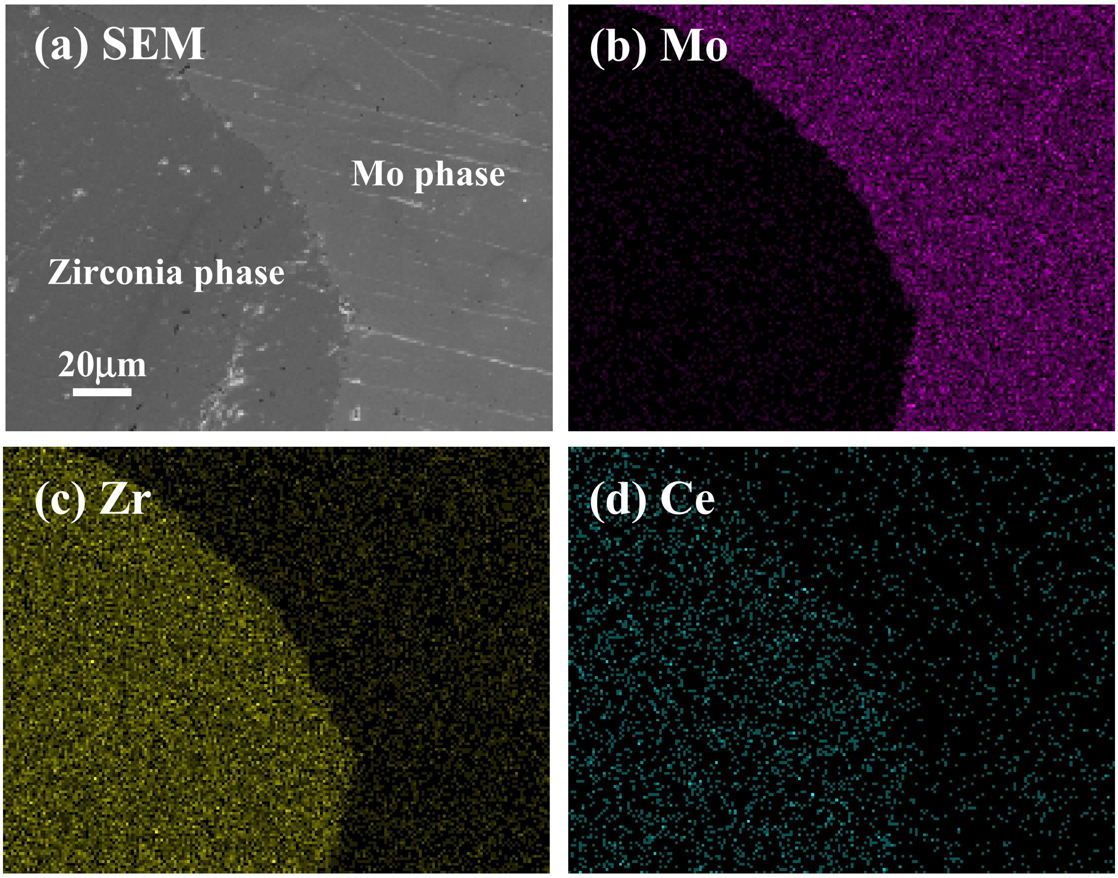

Fig. 8