References

- [1] R. D. Hunt, Jack. L. Collins, Radiochim. Acta, 92(2004)909
- [2] S. S. Pathak, I. C. Pius, R. D. Bhanushali, Mater. Res. Bull., 43(2008)2937.
- [3] R. D. Hunt, R. R. Hickman, J. L. Ladd-Lively, Ann. Nucl. Energy, 69(2014)139.
- [4] R. D. Hunt1, T. B. Lindemer, Radiochim. Acta, 95(2007) 225.
- [5] D. P. Stinton, W. J. Lackey, J. Am. Ceram. Soc., 65(1982)1151.
- [6] R. D. Hunta, G. W. C. M. Silva, J. Nucl. Mater. 427(2012)245.

2 - 31 An Improved Internal Gelation Process for Fabricating CeO₂ Ceramic Microspheres as a Surrogate of PuO₂ Nuclear Fuels

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In this work, an advanced approach is described to simplify the internal gelation process. The chemical kenetics of the internal gelation process is systematically studied by two different methods. The gelation time is affected by three factors: $[OH^-]/[Ce^{4+}]$, $[HMTA]/[Ce^{4+}]$ and temperature (T). The gelation process speeds up when we increase the $[OH^-]/[Ce^{4+}]$, $[HMTA]/[Ce^{4+}]$ and temperature (T). Gels with good property can be achieved by adjusting the $[OH^-]/[Ce^{4+}]$, $[HMTA]/[Ce^{4+}]$. The room temperature stock cerium nitrate solution and HMUR solution were delivered separately by two HPLC pumps and mixed statically in a commercial T-typed mixer just before the drop formation^[1]. This new method was used to prepare cerium oxide microspheres, where the cerium was taken as a surrogate of plutonium. Using the method described above, we also successfully fabricated gelled microspheres even when the stock cerium nitrate solution and HMUR solution are heated up to 50 °C. This method largely shortened the contact time between MA metal solution and HMUR solution, which reduced the radiolysis effect of minor actinides (MA) elements, and it greatly simplified the process of fabricating nuclear fuels containing minor actinides for transmutation. In future, we can combine this new method with the microwave heating technique to study the gelation process within the microwave cavity. All together, it can be potentially used to fabricate transmutation nuclear fuels in glove box for the ADS in China in the future.

I. Chemical kinetics of the internal gelation process

I. A. The effect of the $[OH^-]/[Ce^{4+}]$ on the gelation time of the mixed solutions at 25 °C

The mixed solutions with different $[OH^-]/[Ce^{4+}]$ is prepared at 25 °C for investigating the effect of the $[OH^-]/[Ce^{4+}]$ on the gelation time. The results in Fig. 1(b) show that the gelation time became shorter and shorter with the increase of $[OH^-]/[Ce^{4+}]$, in other words, the mixed solution became easier to gel as the $[OH^-]/[Ce^{4+}]$ increases. This is because the external supply of OH⁻ makes the mixed solution more basic, which is helpful for the hydrolysis of Ce⁴⁺. As the hydrolysis of Ce⁴⁺ going on, the mixed solution became more and more basic. From Fig. 1(a), we can see when the pH is close to 4.0, the mixed solutions start to precipitate, leading to the sharp increase in the viscosity of the mixed solution.



Fig. 1 (color online) The variation in pH (a) and viscosity (b) of the mixed solutions as a function of standing time with different $[OH^-]/[Ce^{4+}]$ at 25 °C; [Urea]/[HMTA] = 1; $[HMTA]/[Ce^{4+}] = 2.44$.

NH₄OH to remove excess HMTA, urea, and ammonium

nitrate. The air dried spheres shrink and have a diam-

eter of 1 mm. The dried spheres were calcined up to

500 °C for 4 h and then sintered up to 900 °C for 2 h

to get phase pure cerium oxide^[2]. The sintered spheres have a diameter of only 600 μ m and their color turn into

yellowish white, which is the same color of cerium oxide.

III. Lattice structure of the sintered spheres

The XRD pattern spectra are assigned to cubic fluoride

structure with a Lattice parameter of 5.40 Å, and the

Miller indices correspond to each identified diffraction

peak. The XRD pattern of the sintered spheres is ex-

actly same as the standard CeO_2 , which means the sintered spheres have a quite pure phase structure.

Fig. 2 shows the XRD pattern of the sintered spheres.

Some of the spheres cracked when they were sintered.

II. Fabrication of CeO_2 by sol-gel process

Using the equipment in our laboratory, CeO_2 spheres were fabricated by internal gelation. Once the mixed broth was dropped into the hot silicone oil, it started to gel immediately, and the color of the broth changed from transparent yellow to semi-translucent yellowish brown. After having aged for 30 min, the gelled spheres were collected in a stainless steel basket. The collected unwashed spheres were then aged in 12.5% (m/m) NH₄OH for 0.5 h, and then the gelled spheres were washed firstly by CCl₄ to remove the silicone oil and then with 0.5 mol/L



Fig. 2 (color online) XRD pattern of sintered spheres.

References

[1] Shigeru Yamagishi, Journal of Nuclear Materials, 14(1998)254.

[2] R. D. Hunta, F. C. Montgomerya, J. L. Collins, Journal of Nuclear Materials, 160(2010)405.

2 - 32 Release and Gathering of Semi-volatile Fission Products (Mo, Te) in the UO₂ Simulated Fuel

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The volatilization technology, which is used for pulverizing uranium oxide ceramic pellets, decladding, and removal of most of volatile and semi-volatile fission elements from spend fuel, has been developing as main treatment process for ADS nuclear fuel cycle. In the oxidation/reduction steps (400 °C to 600 °C), most of the volatile nuclides such as Kr, Xe, C-14, H-3, can be removed. However, the higher temperature is needed to release semi-volatile fission products.

Westphal *et al.*^[1] at INL reported release rates of semi-volatile fission products (Cs, Te, Rh, Tc-99, Ru, Tc, Mo) during oxidation of spent fuel from 500 °C to 1 250 °C. Song *et al.*^[2] at KAERI showed that release rates of Kr-85, C-14 during OREOX process, and the release fraction of semi-volatile Cs was ~16% during a reduction at 1 000 °C of the oxidized powder, but over 90% during the voloxidation at 1 250 °C. From the experimental data by INL and KAERI, and published data^[3,4], *etc*, release rates of Cs is 98% during PRESENT (Particle size control, REmoval of fission product, SElective gaseous Nuclide Trapping) process^[5]. Those of Kr, Xe, H-3, C-14, I-129 are 100%. And, those of Tc, Ru, Rh, Te, Mo and Rb are 92%, 98%, 83%, 53%, 62% and 96%, respectively.

In our present work, the release and gathering of Mo and Te, as two typical elements of semi-volatile fission products, were researched for simulating the volatilization technology. On the basis of the previous studies in the pulverizing process, a small amount of oxides of Mo and Te (MoO₃ and TeO₂) was added in the UO₂ simulated fuel powder and the efficiency of release was researched in different temperatures. As shown in Fig. 1, MoO₃ and TeO₂ both begin to evaporate when the temperature is higher than 800 °C. The rates of release, reached the maximum at 1100 °C ~1200 °C, are 70% and 88%, respectively.

After that, the gathering experiments of MoO_3 and TeO_2 were carried out. The results (Fig. 2) confirmed that, MoO_3 is mainly gathered under 750 °C and TeO_2 under 850 °C. Both the distributed regularity of oxides is strongly influenced by gas, which deposited with the spread of air in the quartz tube.