Solidification of simulated actinides by natural zircon

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Abstract Natural zircon was used as precursor material to produce a zircon waste form bearing 20wt% simulated actinides (Nd_2O_3 and UO_2) through a solid state reaction by a typical synroc fabrication process. The fabricated zircon waste form has relatively good physical properties (density 5.09g/cm^3, open porosity 4.0%, Vickers hardness 715kg/mm^2). The XRD, SEM/EDS and TEM/EDS analyses indicate that there are zircon phases containing waste elements formed through the reaction. The chemical durability and radiation stability are determined by the MCC-1 method and heavy ion irradiation; the results show that the zircon waste form is highly leach resistance and relatively stable under irradiation (amorphous dose 0.7dpa). From this study, the method of using a natural mineral to solidify radioactive waste has proven to be feasible.

Keywords Zircon, Waste form, Solidification, Actinide, Chemical durability, Radiation stability

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1 Introduction

Zircon ($ZrSiO_4$) has always been used as natural analogue for the alpha-decay damage study of ceramic HLW (high level waste) forms. Due to its high resistance to thermal shock, low thermal expansion and extremely durable properties,[1,2] zircon can retain U, Th and their decay products in its mineral crystal structure for geological ages. Therefore it has been proposed as a durable matrix for immobilization and disposal of excess weapon-grade plutonium.[2-4] The synthesis of zircon is difficult because of the relatively small free energy of formation, slow diffusion kinetics, and kinetically large activation energy for the combination reaction between the component oxides (ZrO_2 and SiO_2).[1] Even at high temperature and pressure the synthesis does not result in high yields.[5,6]

Based on the thought "return to the nature", natural zircon is used as the precursor material through the typical synroc fabrication process to facilitate the solid state reaction for incorporating the simulated actinide waste into the zircon waste form. Properties and microstructure of the waste form were analyzed and evaluated in this paper.

2 Experimental

The precursor material used for the synthesis of the zircon waste form was natural zircon from Gansu Province, China. It mainly consisted of zircon with a small amount of SiO_2. The natural zircon was crushed and sieved through a 200 mesh sieve.

The powder was mixed with a nitric acid solution of simulated actinides. Neodymium (Nd) and uranium (U) were used as simulants of trivalent and tetravalent actinides,respectively, with a molar ratio of An^{3+}/An^{4+} of 1/5. The adopted waste loading was 20wt%. The mixture was dried and calcined (at 750℃,for 2h, in 3.5%H_2/N_2 atmosphere), then hot pressed (at 1200℃, 20MPa for 2h, in graphite die) to produce a zircon waste form.

The fabricated sample was cut (10mm×10mm×2mm), polished and cleaned for characterization. The physical properties such as density, open porosity and hardness of the zircon waste form were characterized using a water immersion technique and the Vickers indentation technique. Phase assemblages were determined by a Rigaku D/max–RB X-ray diffractometer (XRD) using Cu K_α (λ=0.15406 nm) radiation.

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The microstructure and phase compositions were studied by a Cambridge S250MK3 scanning electron microscope with Link AN 10000 energy dispersive spectrometer (SEM/EDS) and a Hitachi-800 transmission electron microscope with a PV 9100/75 energy dispersive spectrometer (TEM/EDS). The durability of the sample was tested by the MCC-1 (MCC — Materials Characterization Center, USA) method. The leachate was analyzed by inductive coupled plasma mass spectroscopy (ICP/MS) and the leached surface was investigated by SEM/EDS. The amorphization dose of the zircon was determined after irradiation by a 100 MeV ^{32}S ion beam on the HI-13 Tandem.

3 Results and discussion

3.1 Physical properties

Test results of physical properties were listed in Table 1.

From the results listed in Table 1, one can find that the synthetic zircon waste form has acceptable physical properties.

Table 1 Physical properties of natural zircon and zircon waste form

Samples	Density ($g \cdot cm^{-3}$)	Open porosity (%)	Vickers hardness ($kg \cdot mm^{-2}$)
Natural zircon	5.27	0.51	846
Zircon waste form	5.09	4.0	715

3.2 Phase assemblages and microstructure

The XRD pattern of zircon waste form (Fig.1) indicated that the major phase was zircon, and the minor phase was uraninite (UO_2).

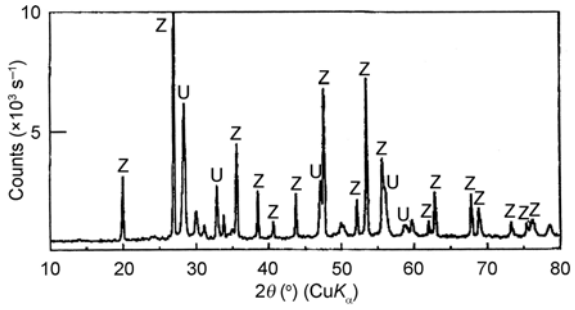

Fig.1 XRD pattern of zircon waste form (Z-Zircon, U-Uraninite).

The SEM and TEM images of zircon waste form were given in Fig.2.

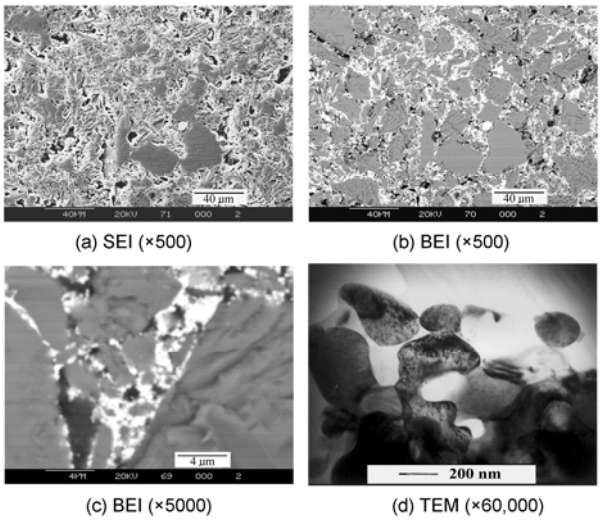

Fig.2 SEM and TEM images of zircon waste form.

Secondary electron image (SEI) showed that the sample had microvoids, in accordance with test results of physical property (Fig.2a). The backscattered electron image (BEI) indicated that there were some zircon grains among the matrix (Fig.2b), and they almost had not participated in the solid state reaction because of their large size (10～100μm). This was one reason that the physical properties of the zircon waste form were not as good as natural zircon. The solid state reaction mainly took place in the matrix between the zircon grains, as can be seen in Fig.2c and Fig.2d. The bright contrast phase is uraninite, the grey phase is zircon, and the black phase is SiO_2. The phase grain size was about 200nm.

The chemical compositions of the phases in the area among the unreacted zircon grains were analyzed by TEM/EDS. The results are shown in Table 2 along with the inferred phase formulae.

The TEM/EDS analysis results confirmed that through the solid state reaction the zircon phase containing the waste elements U and Nd $[(Zr_{0.10}Nd_{0.18}U_{0.60})_{0.88}Si_{1.12}O_4]$ was obtained. The presence of the uraninite phase was due to incomplete reaction with the unreacted zircon grains. Existence of few SiO_2 phases was due to inclusions in the natural zircon.

Table 2 Results of TEM/EDS analyses

Phase	Elemental composition (at. %)				Formula
	Si	Zr	Nd	U	
Zircon(A)	47.70	51.36	0.00	0.95	$(Zr_{1.03}U_{0.02})_{1.05}Si_{0.95}O_4$
Zircon(B)	55.91	5.06	9.05	29.98	$(Zr_{0.10}Nd_{0.18}U_{0.60})_{0.88}Si_{1.12}O_4$
Uraninite	6.73	17.77	8.63	66.87	$(U_{0.67}Zr_{0.18}Nd_{0.09}Si_{0.07})_{1.01}O_2$
SiO_2	95.97	2.00	1.08	0.95	$(Si_{0.96}Zr_{0.02}Nd_{0.01}U_{0.01})_{1.00}O_2$

3.3 Hydrothermal durability

The hydrothermal durability of the zircon waste form was tested by the MCC-1 method (at 90℃, for 3, 7, 14, 28, 90d respecively, in deionized water, $SA/V = 10\ m^{-1}$). The leachate was analyzed for Zr, Nd and U by ICP/MS. The mass and elemental normalized leach rates are listed in Table 3.

The results listed in Table 3 indicated that the fabricated zircon waste form was durable with low mass loss and elemental normalized leach rates compared with typical synroc.[7] The surface of leached samples was tested using XRD and SEM. The SEM images of 7, 14, 28 and 90 day leaching samples are shown in Fig.3. From these four images we found there was no significant alteration on the surface under experimental conditions.

Table 3 Mass and elemental normalized leach rates

Elements	Elemental normalized leach rate ($g \cdot m^{-2} \cdot d^{-1}$)				
	3 d	7 d	14 d	28 d	90 d
Zr	3.24×10^{-6}	1.39×10^{-6}	6.94×10^{-7}	6.94×10^{-7}	2.16×10^{-7}
Nd	1.75×10^{-4}	4.40×10^{-4}	2.33×10^{-4}	1.19×10^{-4}	1.50×10^{-4}
U	2.22×10^{-5}	3.53×10^{-5}	4.00×10^{-5}	1.31×10^{-5}	1.30×10^{-5}
Mass loss	1.80×10^{-1}	1.2×10^{-1}	8.1×10^{-2}	4.8×10^{-2}	1.60×10^{-2}

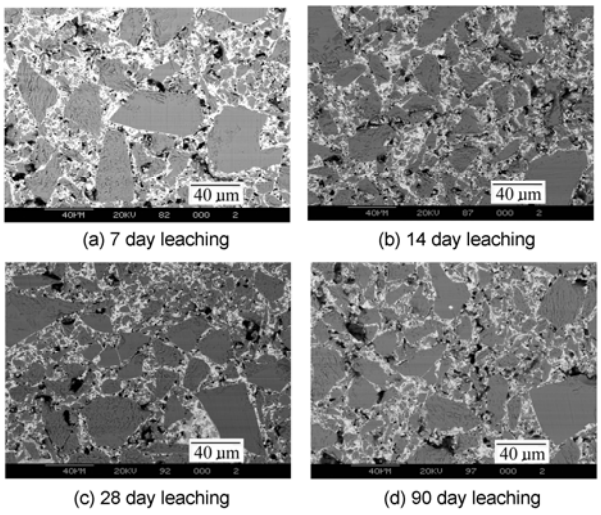

Fig.3 SEM images of leached zircon waste form samples

3.4 Irradiation test

The samples were irradiated by using 100 MeV ^{32}S ion beam from the HI-13 tandem accelerator at National Nuclear Physics Laboratory, China Institute of Atomic Energy (CIAE). The depth of ^{32}S ion implantation was 18.7μm, as calculated by the TRIM-91 program.[8] The adopted ion fluence was $2.46\times10^{11}\ cm^{-2}$, and the irradiation dose rate was 1.62×10^{-4} dpa $\cdot\ s^{-1}$ (dpa: displacement per atom). Samples of the zircon waste form were irradiated up to the dose of 1.6 dpa at room temperature.

The amorphization dose of the zircon waste form was determined by XRD. The highest diffraction intensity I_0, of peak (200), refers to the intensity of an unirradiated sample, while I refers to the intensity of irradiated samples. The figure of I/I_0 with irradiation dose is shown in Fig.4.

From Fig.4, the zircon phase X-ray amorphous state was reached at the irradiation dose of 0.7 dpa. Because unirradiated regions existed, the I/I_0 did not fall to zero. This value is comparable with 0.7dpa of 10wt%^{239}Pu doped zircon[3] and 0.55dpa of 1.5MeV Kr^+ ions irradiated zircon.[9]

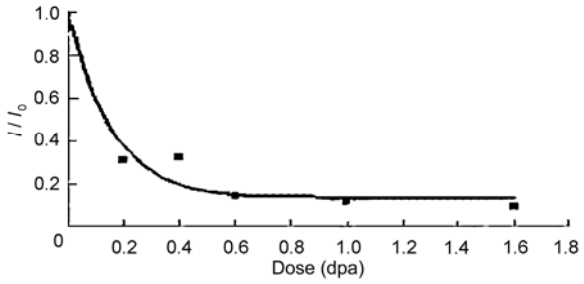

Fig.4 Zircon I/I_0 *vs* irradiation dose

4 Conclusions

The fabrication of a zircon waste form bearing 20wt% simulated actinides using natural zircon powder as precursor material indicated that this fabrication procedure is feasible. Through solid state reaction, the zircon phase containing U and Nd was obtained.

The fabricated zircon waste form had acceptable physical properties including density (5.09 g/cm^3), open porosity (4.0%) and hardness (715 kg/mm^2). It was durable; the elemental normalized leach rate for Nd, U and Zr was 10^{-4}, 10^{-5} and (10^{-6}~10^{-7}) g • m^{-2} • d^{-1}, respectively, and the mass loss rate was (10^{-1}~10^{-2}) g • m^{-2} • d^{-1}. There was no significant alteration on the surfaces under experimental conditions.

The amorphization dose of the zircon waste form was 0.7 dpa, indicating that the zircon waste form was relatively stable under the simulated irradiation condition.

Due to the large grains (>100μm) of natural zircon which inhibited the solid state reaction, properties of the zircon waste form were not good enough. However, the reduction of grain size (<100μm) and adjustments in the fabrication process would improve its properties.

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