

Study of Cerium State in the Process of Self-propagating High-temperature Synthesis

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Abstract. In this paper, thermit was used as the heat source of self-propagating reaction. The main components of sand, Al_2O_3 and SiO_2 were selected as the curing materials with adding 5% CeO_2 as the simulated nuclide. The reaction process of simulated nuclide at high temperature and the existing form in the solidification were analysed and characterized by TG-DSC and XRD. The results showed that the obtained solidifications were amorphous glass and ceramic phases. In the Al_2O_3 and CeO_2 system, the reaction temperature was 1320°C , and Ce was mainly in the form of $\text{CeAl}_{11}\text{O}_{18}$ in the solidification. In the system of SiO_2 and CeO_2 , the reaction temperature was 1280°C , and Ce was mainly in the form of Ce_2SiO_5 in the solidification.

1. Introduction

For radioactive waste, no matter what curing technology is applied, it will face the scientific problem of the existence of nuclides in the solidified body. What is the valence state of the nuclide, and what is the existence of the phase, and whether it is mechanically wrapped in other phase or in the form of lattice substitution in the main crystal phase, which will directly affect the curing properties of the nuclides, such as the leaching rate of the nuclides^[1-3]. At present, domestic and foreign scholars generally agree that nuclides should be dissolved in the main crystal phase by lattice substitution. Self-propagating high-temperature synthesis (SHS) is a new technology that uses chemical reactions exotherm to make the reaction continuously to produce the necessary materials or products. In recent years, the application of SHS technology has gradually expanded from the field of new material synthesis to the radioactive waste solidification^[4-6]. The technology is mixing the metal powder fuel with the radioactive waste, and uses the heat released by the SHS to melt the waste, eventually consolidating the radioactive nuclides into the curing products. For the treatment of solid radioactive waste, SHS technology has some technical and cost advantages, for example: (1) lower energy consumption, no large expensive equipment; (2) directly applied to waste disposal point or local disposal; (3) higher synthesis temperature which could melt more harmful substances; (4) faster reaction rate, higher treatment efficiency, and less aerosol formation at high temperatures^[7,8].

This paper selected Al powder and Fe_2O_3 mixture as the SHS reaction material system, and used the rare earth element Ce as the simulated nuclide. The main components of sand mixed tracer Ce were selected as simulated radioactive waste. The conditions of the reaction were analyzed, and the porosity and volume density of the products were analyzed. And the crystal phase of the structure was analyzed.



2. Experimental procedures

2.1. Sample preparation

Al and Fe₂O₃ were selected as self-propagating materials, and Al₂O₃ and SiO₂ with a certain proportion of tracer CeO₂ were used as simulated radioactive sand. The properties of the raw materials are shown in Table 1.

Table 1 Properties of raw material powders

Raw material	Al	Fe ₂ O ₃	CeO ₂	Al ₂ O ₃	SiO ₂
Mass fraction /%	98	98	99	99	99
Particle size / μm	<50	<40	<40	<100	<100

First, the Al and Fe₂O₃ were mixed according to the thermit stoichiometric ratio. Then, Al₂O₃, SiO₂ and CeO₂ were added separately. The mass fraction of the raw material is shown in Table 2.

Table 2 Experimental mass ratio of raw materials

Sample	Mass ratio /%			
	Thermit	Al ₂ O ₃	SiO ₂	CeO ₂
A	47.5	47.5		5
B	47.5		47.5	5

In order to make the reactant fully contact, promote the mutual reaction between the materials, and realize reduction of the radioactive waste in the process of treatment and disposal. The powder sample was pressed before the SHS. The powder samples were granulated by adding ethylene glycol, and then pressed under 10MPa for 3min, and finally put it into an electric drying oven at 110 °C for 3h to remove ethylene glycol. The sample was placed in a high temperature atmosphere tube furnace to SHS experiment. Before heating up, the vacuum and argon filling were performed three times in turn to remove the air in the tube furnace to avoid the Al oxide in the process of heating. Under the protection of argon, the samples were heated to 1450 °C at 10 °C/min. After the tube cooling, the solidified bodies were obtained from the reaction. The appearance of the sample A from the powder to the pressed sheet finally becomes the solidified body were shown in Figure 1.

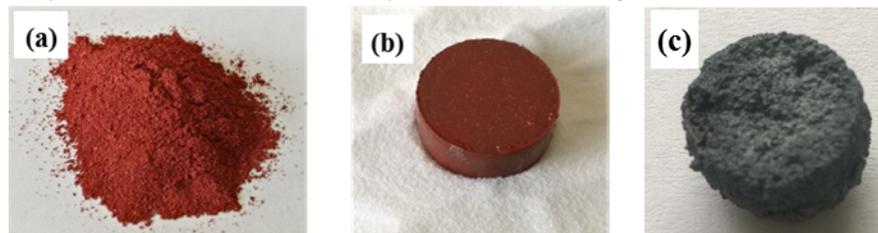


Fig. 1 The appearance of sample A before and after treatment (a) after batching, (b) after pressing, (c) solidified body

2.2. Analysis and characterization

According to the national standard GB/T9966.3-2001 "The porosity and bulk density test method of porous ceramics", the volume density and the porosity of the obtained solidified body are measured. The calculation formula is as follows:

$$q = \frac{G_2 - G_1}{G_2 - G_3} \times 100 \quad (1)$$

$$D_v = \frac{G_2}{G_2 - G_3} \times 100 \quad (2)$$

Where, q is the apparent porosity of the sample (%); D_v is sample volume density (g/cm^3); G_1 is the dry mass of the sample (g); G_2 is the mass in the air after the sample is saturated with water; G_3 is the mass of the saturated sample in the water (g).

The TG-DSC analysis of the powder before the curing reaction was carried out by using the synchronous heat analyser(STA449F3, Netzsch, German). Under the protection of argon, the temperature of the curing reaction of the sample was analysed with the heating rate of 10 °C /min to 1450 °C. The structure of the solidified body and the existence form of simulated nuclides were analysed by X-ray diffractometer(D8 Advance, Bruker AXS, German). The working voltage of the diffractometer is 40KV, the current is 40mA, and the diffraction angle is 10-85° with diffraction rate of 5°/min.

3. Results and analysis

3.1. DSC Analysis

After mixing the raw materials in proportion according to the table 2, the sample A and sample B were analyzed and characterized by using the synchronous heat analyzer. The analysis results were shown in Figure 2.

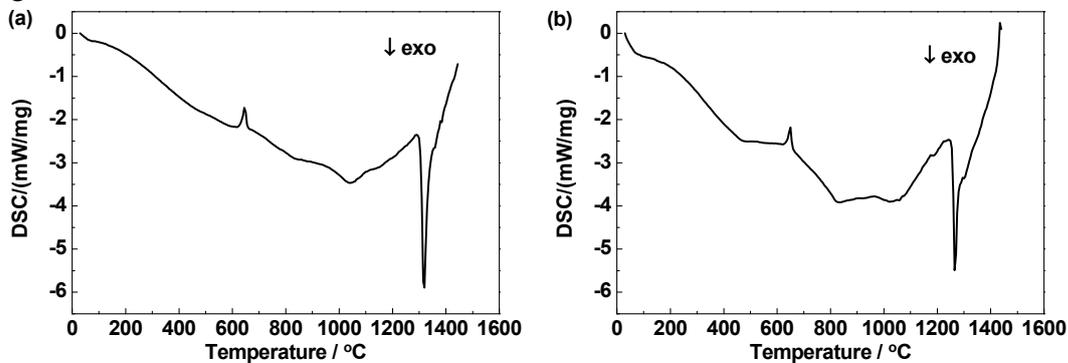


Fig. 2 Thermal analysis curve (a) sample A, (b) sample B

Fig.2(a) and (b) both present the first endothermic peak at 650°C, because the aluminum powder begins to melt and absorb heat during heating. In the high temperature stage, there is a relatively intense exothermic peak generated by SHS. From the exothermic peak, it can be seen that both sample A and sample B had SHS reaction. It shows that the SHS could play the role of solidifying radioactive waste.

From Fig2 (a), it can be seen that after adding Al and CeO₂, the temperature of the beginning of the SHS starting temperature changes comparing to the pure thermit, and the starting temperature was at 1320°C. From Fig.2(b), it can be seen that the exothermic peak of adding SiO₂ and CeO₂ in the thermit with Ar gas protection appeared at 1280°C.

3.2. Apparent morphology analysis

The apparent porosity and bulk density of the samples were tested and the results were shown in Table 3. The physical appearance of the samples after SHS reaction were shown in Fig.3

Table 3 Apparent porosities and densities of waste forms

Sample	Apparent porosity /%	Density /(g · cm ⁻³)
A	4.82	3.37
B	5.04	3.26

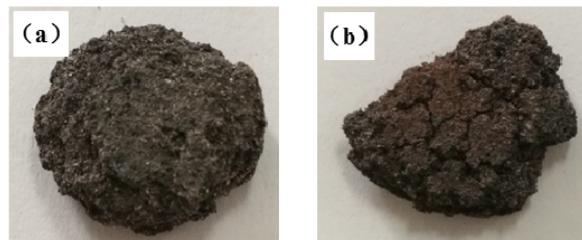


Fig.3 Photos of samples after SHS reaction (a) Sample A; (b) Sample B

Under the condition of natural combustion, the SHS reaction products are loose and porous, and the apparent porosity can be up to 16%, and the bulk density is between $2.4\sim 2.8\text{ g/cm}^3$. In order to reduce the porosity of the product and improve the mechanical properties of the solidified body, the powder sample was pressed before the high temperature reaction. The apparent porosity of the solidified body was controlled to about 5%, and the volume density was raised to around 3.3g/cm^3 . This indicates that pressing the powder sample before high temperature reaction can effectively reduce the apparent porosity of the solidified body and increase the volume density of the product.

3.3. XRD analysis

In order to study the chemical reaction of the nuclide during SHS and the presence of tracer in the solidified body, the XRD analysis of the solidified body was carried out. The results were shown in Fig.4.

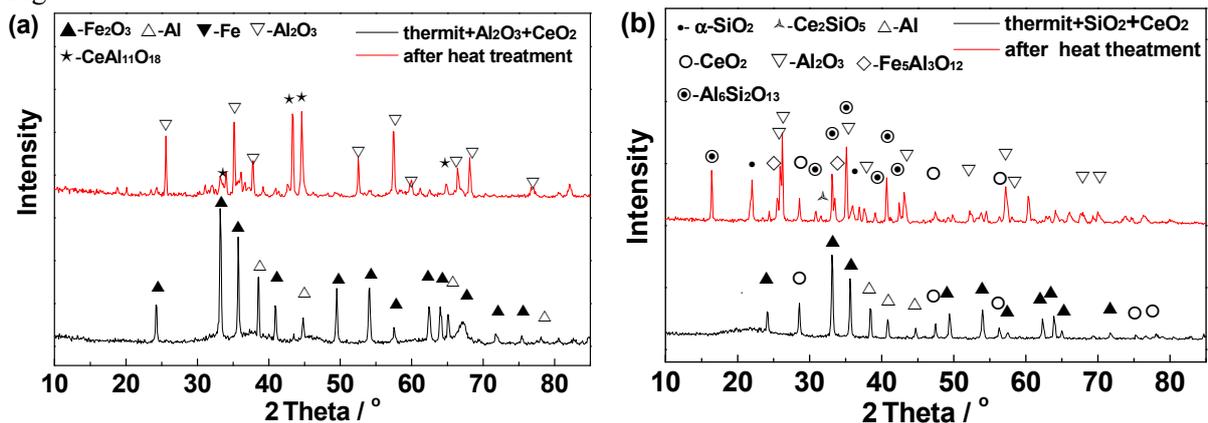


Fig.4 XRD diffraction pattern before and after SHS of the samples

(a) Sample A; (b) Sample B

It can be seen from Fig.4(a) that after the high temperature reaction, the diffraction peaks of Fe_2O_3 and Al disappeared and the Al_2O_3 diffraction peaks appeared. It was observed that $\text{CeAl}_{11}\text{O}_{18}$ peak appeared at $2\theta=44^\circ$ and $2\theta=46^\circ$ after heat treatment, which indicated that the simulated nuclide was involved in the curing reaction at high temperature and Ce existed in the form of $\text{CeAl}_{11}\text{O}_{18}$ in the solidified body. At the same time, no metal cerium was observed from the XRD diffraction pattern. It is observed from Fig.4(b) that there were the diffraction peaks of Al and Fe_2O_3 before the high temperature reaction. After the addition of SiO_2 , CeO_2 and high temperature reaction, the diffraction peak of Ce_2SiO_5 appeared at $2\theta=32^\circ$, and the diffraction peaks of $\text{Al}_6\text{Si}_2\text{O}_{13}$ appeared in the solidified body, which indicated that the addition of SiO_2 at high temperature makes the reaction in the solidified body more complicated^[9].

It is observed from Fig.4 that the solidified body is a mixture of amorphous glass and ceramics. The simulated nuclide Ce was involved in the oxidation-reduction at high temperature and the new structure of Ce was mainly in the presence of $\text{CeAl}_{11}\text{O}_{18}$ and Ce_2SiO_5 through combination of Ce and other substances. Zec and Kepinski^[10,11] studied the reaction of CeO_2 and SiO_2 powder in the air and it was found that when the sintering temperature reached 1100°C , the XRD spectra of the products changed significantly and the diffraction peak of Ce_2SiO_5 appeared. Kepinski also analysed the phase

diagram of $\text{CeO}_2\text{-SiO}_2$ and it was observed that several cerium silicates can be formed at atmospheric pressure, such as Ce_2SiO_5 , $\text{Ce}_2\text{Si}_2\text{O}_7$ and CeSiO_4 . The formation of these structures is closely related to the sintering temperature and reaction atmosphere. Therefore, the thermal stability of $\text{CeAl}_{11}\text{O}_{18}$ and Ce_2SiO_5 in the solidification products needs further study.

4. Conclusions

1. It is feasible to initiate SHS by heating thermit in inert atmosphere. The combustion heat of the thermit is very high, and it can melt the sand containing simulated nuclides into a mixture of amorphous glass and ceramic phase.

2. After Al_2O_3 is added to the thermit, the temperature of SHS occurs at $1320\text{ }^\circ\text{C}$. The simulated nuclide Ce exists mainly in the form of $\text{CeAl}_{11}\text{O}_{18}$ in the solidified body.

3. After SiO_2 is added to the thermit, the temperature of SHS occurred at $1280\text{ }^\circ\text{C}$. The simulated nuclide Ce exists mainly in the form of Ce_2SiO_5 in the solidification product.

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