Synthesis of Multiphase SYNROC Powders as a High Level Radioactive Waste Ceramic Forms by a Solution Combustion Synthesis

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1. Introduction

Synthetic rock (SYNROC) is a titanate-based ceramic assemblage containing four major phases: perovskite ($CaTiO_3$), zirconolite ($CaZrTi_2O_7$), hollandite (ideal formula $BaAl_2Ti_6O_{16}$) and rutile TiO_2 [1]. These minerals have the capacity to accept nearly all of the elements present in the high-level nuclear waste (radwaste) produced during the reprocessing of spent nuclear fuel rods of nuclear reactors. Synroc minerals can accommodate up to 20 wt% (as oxide) of radwaste in their crystal lattices as dilute solid solutions. Synroc-B refers to the waste free composition, proposed for the immobilization of nuclear wastes generated in the commerical nuclear power plants, while the waste-loaded synroc is called synroc-C [2].

The oxide-route (solid state reaction) with high temperatures and long sintering times is the most known process to form a solid solution. [3-5] However, the synthesis of nano powders using an exothermic redox reaction between nitrate and organics in an aqueous solution has been reported. [6,7] Most of the high-level radioactive wastes forms were dissolved in nitric acid, and therefore the solution combustion synthesis (hereafter called SCS) which uses all of the metal nitrates as reactant materials is a very promising process to immobilize the radioactive metal element wastes in the form of solid solutions. During the combustion, a significant volume of gas evolved and the high temperature inherent to the highly exothermic nature led to fine and homogeneous well-crystallized powder within a short reaction time. Patil et al. reported that Synroc-B has a waste-free composition proposed for the immobilization of nuclear wastes, and can be prepared through combustion processes using carbohydrazide and tetraformal trisazine as fuels. [6]

In this study, the SCS and oxide route was compared to form the solid solution of Synroc-B nano powders.

2. Methods and Results

2.1 Experimental

The composition of Synroc-B powder made by oxide-route is shown in Table. 1. The 3D-wet milling was used to mix of each components of Synroc-B, and after then it was dried and calcined at 1100℃ for 2h.

In the case of SCS, Ca, Zr, Al and Ba nitrate and $TiO(NO_3)_2\ xH_2O$ were used as the source materials. Titanium nitrate was not commercially available, and was prepared from $TiCl_4$ according to the previous reported procedures. [7] To investigate the effect of fuel on the combustion reaction, the stoichiometric composition of glycine (NH_2-CH_2-COOH) was calculated according to the method of Jain et al. [8] which denotes a fuel to metal nitrate ratio at which the fuel can react completely with all of the metal nitrates, such that no residual fuel or nitrate remains in the final product.

After this metal salt and fuel were dissolved in 100ml of deionized water, the precursor solution was stirred and heated on a hot plate. As soon as the water became fully vaporized, spontaneous combustion occurred through the burning of metal salt and fuel. The synthesized powders were characterized by DTA/TGA, XRD, SEM and TEM/Mapping.

Table.1 Components in Synroc-B and the composition of the constituent oxides.

Component Synroc-B		Minerlogy	
Oxide	wt%	Composition	wt%
TiO_2	71.4	Hollandite($BaAl_2Ti_6O_{16}$)	30
ZrO_2	6.76	Zirconolite($CazrTi_2O_7$)	30
Al_2O_3	5.38	Perovskite($CaTiO_3$)	20
BaO	5.31	Magnell phase(TiO_2)	15
CaO	11.15	Intermeralilics	5

2.2 Result and Discussion

Combustion synthesis performed without external energy supply because the flame of reaction during the combustion process is directly used as an internal energy source. The overall process reaction is preceded by the chemical reaction between oxidizer and fuel, where the elements such as C, H and O of amino acid act as a fuel, and the element oxygen of metal nitrate acts as an oxidizer. Generally, the combustion process produces homogeneous phases with excellent crystallinity owing to the high temperature arising from the drastic exothermal reaction.

The crystallization behavior of the synthesized Synroc-B powders with various heating temperatures is shown in Fig. 1. The crystallization of as-synthesized combustioned Synroc-B powder (Fig. 1(a)) has three

component (perovskite(P),hollandite(H),zirconolite(Z)), but the crystallity is not perfectly conformed up to 900℃. The results of as-synthesized powders calcined at 1100℃ for 3h, it does not contain 2nd phase and have highly crystallity with P, H and Z phase. Fig. 1(b) shows the results of XRD patterns with difference preparation route; oxide route and combustion synthesis. In oxide-route, as-synthesized powder were observed of three composition main peaks (P, Z and T), and was almost not detected of the main phase hollandte peak. But as-synthesized in the case of combustion process, main component of Synroc-B was observed as almost identical of the Synroc-B composition.

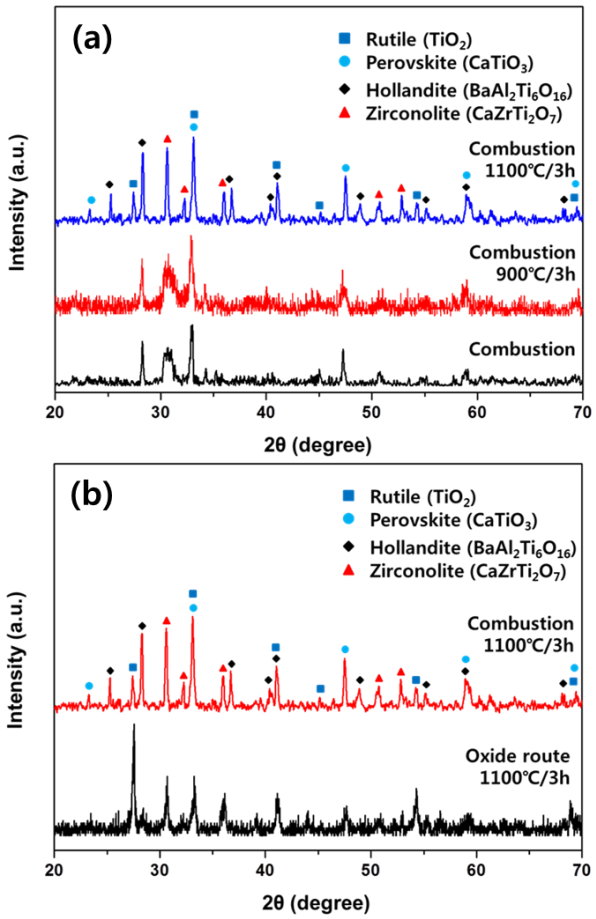

Fig. 1. XRD patterns of Synthesized Synroc-B powders (a) different heating temperature and (b) different synthesized condition

SEM morphologies of the as-synthesized powder prepared by oxide route and combustion synthesis one is shown in Fig. 2. Oxide route as-synthesized Synroc-B powders (Fig. 2(a)) consist of small particles (Ti-O) and big particles (Al-O, Ca-O or Zr-O) according to the result of SEM/EDS. The morphologies of oxide-route particles showed a large, non-uniformed size. However, the nature of the combustion reaction is revealed in the morphologies of Fig. 2(b) of the as-synthesized Synroc-B powder. In this combustion synthesized condition, continuous porous agglomerates are formed. Pore and voids can be seen, which result from the escaping gas. This type of porous network is typical of the combustion of synthesized powders. The primary particle size of as-synthesized powders is about 20~30 nm, which can be correlated with the flame temperature reached during the combustion reaction.

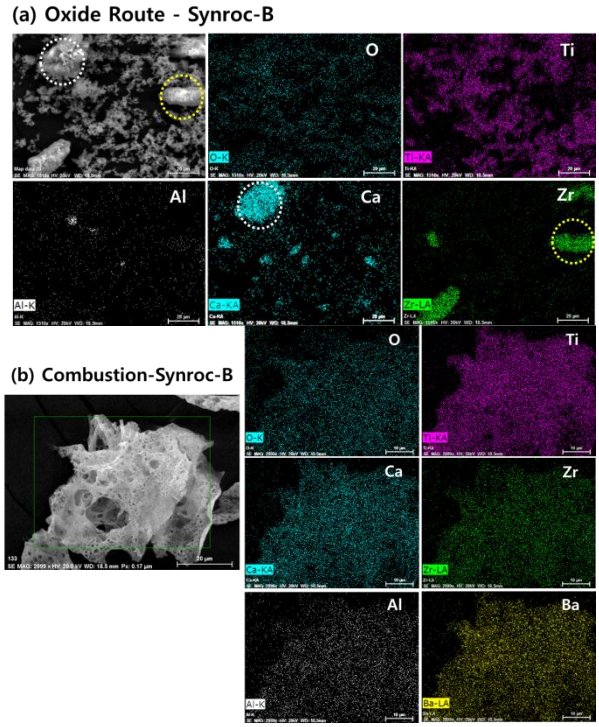

Fig. 2. SEM morphologies and mapping of (a) as-synthesized Oxide route of Synroc-B powder (b) as-synthesized Solution Combustion synthesis of Synroc-B powder

3. Conclusions

The following conclusions were obtained by comparing the combustion synthesis with the oxide route synthesized Synroc-B powders. With Oxide route synthesized synthesis through a wet ball milling and with a calcination temperature at 1100℃, the synthesized particles do not match the Synroc-B composition. It was determined to be a heterogeneous particle size showed about 1μm.

However, Synroc-B particles prepared by combustion synthesis showed all Hollandite, Zirconolite, Perovskite and Rutile structures having a configuration of the complete Synroc-B at a calcination temperature of 1100℃. SEM/EDS Mapping analyses also show that particle size is very homogeneous and evenly distributed in 20 ~ 30nm.

By a combustion synthesis method Synroc-B nano powder of a multi-phase can be produced in a relatively easy way. Solidified in the Synroc-B complex, radioactive elements contained in the high-level radioactive waste can be easily immobilized.

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