

PII S0025-5408(96)00131-6

SINTERING, MICROSTRUCTURAL AND DILATOMETRIC STUDIES OF COMBUSTION SYNTHESIZED SYNROC PHASES

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(Communicated by C.N.R. Rao) (Received April 27, 1996; Accepted May 24, 1996)

ABSTRACT

Sintering, microstructure, and linear thermal expansion properties of Synroc-B and constituent phases, viz. perovskite CaTiO₃, zirconolite ZrTi₂O₇, hollandite (ideal formula BaAl2Ti₆O₁₆) have been investigated. Synroc-B powder when pelletized and sintered at 1250°C for 2 h achieved >95% theoretical density. Sintered Synroc-B has a linear thermal expansion coefficient α of 8.72 × 10⁶ K⁻¹ and Vicker's microhardness 9.88 GPa. The linear thermal expansion curves did not show any hystersis indicating the absence of microcracking in the sintered bodies.

KEYWORDS: A. ceramics, A. oxides, B. chemical synthesis, D. microstructure, D. thermal expansion

INTRODUCTION

Synroc, an assemblage of multimineral phases (perovskite, zirconolite, and hollandite with small amount of rutile TiO_2) has been proposed for the immobilization and permanent disposal of radioactive wastes generated during reprocessing of spent nuclear reactor fuels (1). Synroc minerals occur naturally and have survived in a wide range of geological and geochemical environments for thousands of years, which suggests that Synroc would provide a superior method of immobilizing high level radioactive wastes (HLW) (2).

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Synroc-B refers to the waste-free composition proposed for the immobilization of nuclear wastes generated in the commercial nuclear power plant, and the waste-loaded Synroc is called Synroc-C (3). Various preparation routes, such as Sandia route and hydroxide route (4), have been reported for Synroc-B production, and interest is focused on new, cost-effective preparation routes with better properties.

In continuation of our studies on the solution combustion process of nuclear waste immobilization materials (5,6), we now report sintering, microstructure, and dilatometric results of Synroc-B and its constituents. Thermomechanical properties and thermal expansion are critical for designing Synroc with improved resistivity to leaching and determining displacements and stresses.

EXPERIMENTAL

Synroc phases (perovskite CaTiO₃, zirconolite CaZrTi₂O₇ and hollandite Ba_{1,23}Al_{2,46}Ti_{5,54}O₁₆) and the Synroc-B (1) powders were prepared by solution combustion process using corresponding metal nitrates and fuel carbohydrazide (CH) / tetraformal trisazine (TFTA) at 450°C. Detailed calculation of redox compositions for combustion are described elsewhere (5). TFTA was used as a fuel for the synthesis of calcium titanate. CH was used as a fuel for others. Barium hollandite and Synroc-B powders were prepared under fuel-lean condition (O/F = 2) in order to avoid the volatilization of barium during combustion (6).

Combustion-derived products have been characterized by powder XRD recorded with a Shimadzu XD-D1 X-ray diffractometer with Ni-filtered Cu-K α radiation. For the phase evolution study, the powders were calcined in alumina boats at various temperatures in air, with a soaking period of 2 h, and the phases were identified using the characteristic X-ray reflections.

The combustion derived powders were ground and unaxially pressed (50 MPa) to compacts of diameter 10 mm and thickness 7-8 mm. Polyvinyl alcohol (5% aqueous solution) was used as binder and the binder was removed by heating the pellets at 700°C for 30 min. Sintering of the pellets were carried out at desired temperatures in air with the heating rate of 10°C/min and soaking period of 2 h. The bulk density and open porosity of the sintered pellets were measured using the Archimedes liquid displacement technique. Microstructures of sintered pellets were studied using a scanning electron microscope (SEM, Model S-150 Stereoscan, Cambridge Physical Sciences, Cambridge, UK). The samples were chemically etched in 1:1 solution of 0.5N HNO₃ and 0.8N orthophosphoric acid for 30 sec and then thermally etched at temperatures 200°C less than the sintering temperatures for the microstructural studies. Vicker's microhardness of sintered pellets was measured with a Shimadzu microhardness instrument (model HMV 2000) by applying a load of 100-200 g. The linear thermal expansion of sintered pellets (7-8 mm height and 9-10 mm dia.) was measured using a homemade dilatometer (with quartz push rod and LVDT set-up) in the temperature range of 293-1000 K, with a heating rate of 2°C/min. The dilatometer was calibrated with a NBS standard reference sapphire (SRM 732).

RESULTS AND DISCUSSION

The XRD patterns of the combustion derived Synroc-B and its constituents are shown in Figure 1. The as-formed calcium titanate (Fig. 1a) shows considerable line-broadening,

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Powder XRD patterns of (a) CaTiO₃ (as-prepared), (b) CaZrTi₂O₇ (1000°C, 2 h), (c) Ba-Hollandite (1150°C, 2 h), and (d) Synroc-B (1100°C, 2 h).

indicating the presence of nanosize crystallites ($D_{002} = 27.7$ nm). In the case of calcium zirconolite, the as-formed powder is amorphous with weakly crystalline anatase TiO₂ and t-ZrO₂. Perovskite CaTiO₃ is seen as intermediate phase during the crystallization of CaZrTi₂O₇ phase which completes on calcination at 1000°C (Fig. 1b) (5). As-formed hollandite powder shows very weak peaks corresponding to barium hollandite, barium titanate (BaTiO₃), anatase, and rutile TiO₂. Intensity of BaTiO₃ peaks increases rapidly and attains a maximum at 800°C calcination temperature and then decreases at a faster rate. Above 800°C, the barium hollandite peaks begin to increase rapidly and single-phase barium hollandite is formed on calcination at 1150°C (Fig. 1c).

The evolution of various phases, on calicination at various temperatures, in combustionsynthesized Synroc-B has been reported elsewhere (6). The complete Synroc-phase assemblage formation occurred on calcination at 1100°C for 2 h (Fig. 1d). The XRD pattern shows the presence of all of the Synroc phases.

The theoretical density of combustion synthesized Synroc-B was calculated from the quantitative X-ray analyses. The composition of Synroc-B in terms of weight percentage, as

	Perovskite	Zirconolite	Hollandite	Synroc-B
Pressing load (MPa)	50	50	50	50
Sintering temperature (°C)	1200	1250	1250	1250
Sintering time (h)	1	2	2	2
Density* (g/cm ³)	3.70 (92)	4.35 (98)	4.15 (96)	4.08 (95)
Apparent open porosity (%)	0.25	0.002	0.18	0.20
Vicker's hardness (GPa)	6.15	9.83	4.58	9.88
Thermal expansivity α (× 10 ⁻⁶ K ⁻¹) (RT to 1000 K)	10.80	9.04	8.30	8.72

TABLE 1 Sintering Conditions and Mechanical Properties

* Values in the parentheses are percentage theoretical density.











FIG. 2

Scanning electron micrographs of fracture surface: (a) $CaTiO_3$ (1200°C), (b) $CaZrTi_2O_7$ (1250°C), and (c) Ba–Hollandite (1250°C).



FIG. 3

Energy dispersive X-ray spectra of Synroc-B: I = calcium titanate, II = calcium zirconolite, III = Ba-Hollandite.

observed from the relative XRD peak intensities, is perovskite $(CaTiO_3) = 13$, calcium zirconolite $(CaZrTi_2O_7) = 33$, barium hollandite $(Ba_{1\,23}Al_{2\,46}Ti_{5\,54}O_{16}) = 40$, and rutile $TiO_2 = 13$. Theoretical density calculated for the above composition is 4.31 g/cm³.

Sintering conditions for all of the combustion-derived products are given in Table 1. The combustion-derived products could be sintered to high density at lower temperatures, indicating the reactive nature of the combustion-derived powders. Calcium titanate sintered to 92% theoretical density at 1200°C for 2 h. Increasing the sintering temperature reduces the density, probably due to grain boundary cracking which occurs on cooling through a phase transformation at 1240°C.

<u></u>	Grain (atom %)			
Element	l perovskite	II zirconoloite	ll1 hollandite	
Ca	41.84 (50)	20.13 (25)	~4.26	
Ba	~3.42	~6.20	13.48 (13.33)	
Al	~1.79	~2.50	20.00 (26.65)	
Zr	~4.74	15.38 (25)	~6.24	
Ti	48.21 (50)	55.79 (50)	56.01 (60.02)	

TABLE 2Elemental Analysis (Normalized) from EDX (Fig. 3)*

* Values in the parentheses are ideal cation percentage for respective phases.



Linear thermal expansion plots of $CaTiO_3$ (P), $CaZrTi_2O_7$ (Z), Ba–Hollandite (H), and Synroc-B (S).

The scanning electron micrographs of sintered Synroc phases are shown in Figure 2. The micrographs of CaTiO₃ reveals the presence of pores and cavities, and the grain sizes are in the range of 2–3 μ m (Fig. 2a). The fractograph of calcium zirconolite shows a highly dense nature (98% theoretical density) of the sintered body with well-connected grains (Fig. 2b). Barium hollandite consists of anisotropic elongated grains, as shown by the SEM (Fig. 2c). Synroc-B could be sintered to a density of 4.08 g/c³ (95% theoretical) at 1250°C, 2 h, and the apparent open porosity is 0.2%. The micrograph of Synroc-B confirms the presence of well-mixed Synroc phases.

Individual Synroc phases in Synroc-B have been identified using energy dispersive X-ray analyses (EDX) done on the fracture surface of the sintered pellet, and the results are shown in Figure 3. The elemental analysis using EDX shows that the hollandite grains are elongated, the perovskite grains are spherical, and the zirconolite grains are nearly spherical in shape. Quantitative elemental analysis (normalized) of energy dispersive X-ray spectrum (using ZAFA/FLS software) shows the presence of a small amount of elements other than the stoichiometric compositions (Table 2). This could be due to a small amount of atomic substitutions between the phases or may be due to adjacent grains because the grain sizes are small $(2-4 \mu m)$.

The Vicker's microhardness was measured for all the Synroc phases and for Synroc-B and the values are given in Table 1. The microhardness value of Synroc-B (9.88 GPa) is very close to that of calcium zirconolite. Hollandite is the softest among the Synroc phases, with the microhardness value of 4.58 GPa

The dilatometric curves of Synroc phases and Synroc-B (Fig. 4) are all linear. The linear thermal expansion coefficients (α) of calcium titanate, calcium zirconolite, Ba-hollandite, and Synroc-B are given in Table 1. Among the Synroc phases, calcium titanate has the higher value ($\alpha = 10.8 \times 10^{-6} \text{ K}^{-1}$) compared to barium hollandite ($\alpha = 8.3 \times 10^{-6} \text{ K}^{-1}$). The linear thermal expansion coefficient of Synroc-B ($\alpha = 8.72 \times 10^{-6} \text{ K}^{-1}$) lies in between those of the zirconolite and hollandite phases, major constituents of Synroc-B. The weighed average of α for Synroc-B ($8.79 \times 10^{-6} \text{ K}^{-1}$), calculated using the composition calculated from quantitative XRD analysis, agrees well with the observed value. The linear thermal

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expansion coefficient (α) for r-TiO₂ is taken as 9.6 × 10- K⁻¹ (4). The absence of hysteresis between heating and cooling curves indicates that there is no microcraking in the internal structure of Synroc phases and Synroc-B. Also, it has been observed that there is no change in the linear thermal expansion coefficient values between first and second thermal cycles. This is not very surprising, because the grain sizes are almost always between 1–3 µm for the constituent phases. Microcracking is known to exist in multi-phase compositions due to thermal expansion mismatch, and if grain sizes are sufficiently big. In the present method of synthesis the product obtained is invariably fine grained and, hence, microcracking is avoided.

CONCLUSIONS

The waste-free Synroc powder could be consolidated to high density (>95% theroretical density) with a low apparent open porosity (0.2%) by coventional cold-pressing and atmospheric sintering at temperatures as low as 1250°C, 2 h. The linear thermal expansion coefficient of Synroc-B ($\alpha = 8.72 \times 10^{-6} \text{ K}^{-1}$) is less than the value reported in the literature (7) but the microhardness value is comparable (4). Dilatometric studies of Synroc phases and Synroc-B show that there is no microcracking during conventional sintering of combustion-derived Synroc powders and also no change in the expansion coefficient values between first and subsequent thermal cycles.

ACKNOWLEDGMENT

The authors thank Mr. Sam Philip for the EDX analysis, and one of the authors (MM) is grateful to the Council of Scientific and Industrial Research (CSIR), New Delhi, India, for the award of a Junior Research Fellowship.

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