DEMONSTRATION OF THE FEASIBILITY OF SUBSOLIDUS SINTERING OF RADWASTE-CONTAINING SYNROC-B COMPOSITION

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Technically dense ceramic forms of Ringwood's SYNROC-B, with and without 10 wt% simulated radwaste additions, have been produced on a laboratory scale by ceramic processing, including

1. powder preparation

2. compaction

3. precalcination

4. solid-state sintering.

This silica-free, three-phase mineral assemblage had hitherto been known only in coarse-grained, hot-pressed form; for prepared compacts having $D_0 \approx 0.62$, sintering was complete $(D > 0.95)$ at ~1200 to 1220°C, i.e., more than 100°C below the temperature reported for hot pressing. Under sintering conditions, no loss of radwaste volatiles (e.g., oxides of cesium, strontium, and molybdenum) was discernable gravimetrically; the immobilizing phases (hollandite, perovskite, zirconolite) were well formed in a heterogeneous but very fine-grained (~1 to 3 μm) crystalline microstructure.

I. INTRODUCTION

A sintered SYNROC-B ceramic material has been prepared, which successfully incorporates 10% simulated radwaste material into the three major host phases of SYNROC-B originally described in hot pressed form by Ringwood et al.[1] Using ordinary reagent-grade oxide and carbonate starting materials and nitrate-derived simulated radwaste (AEC-PW-4b) (Ref. 2), a prepared material containing up to 10% radwaste and consisting in final form principally of hollandite, perovskite, and zirconolite was successfully sintered to a fractional density $\gtrsim 0.95$ (4.12 to 4.22 g/cm^3) when fired in a reducing atmosphere in a two-step cycle that included in final 8-h soak at 1220°C.

II. FORMATION OF PRINCIPAL PHASES

The SYNROC-B matrix composition[1] initially investigated was 10% Al_2O_3, 9% CaO, 13% BaO, 57% TiO_2, and 11% ZrO_2; the CaO and BaO were added as carbonates, all the others as reagent-grade oxides. The SYNROC-B matrix powder was prepared by a dry process method described elsewhere[3,4]; the matrix raw materials were subjected to intensive dry ball milling for 6 h, then binder (5 wt% Carbowax 4000) and lubricant (5 wt% isostearic acid) were added in two subsequent remilling stages (6 h each). The powder obtained was relatively free flowing and could be dry pressed at 345 MPa to obtain a starting density of ~0.62 of theoretical (after binder burnout and carbonate breakdown). An x-ray spectrum for the initial matrix material (prior to sintering) is shown in Fig. 1.

Nominal but multiphase specimens approximating the compositions (again, according to Ref. 1) of pure hollandite (H), perovskite (P), and zirconolite (Z), respectively, were also fabricated and fired to observe formation of the individual phases, and to provide tentative x-ray standards for these phases (Fig. 1). (In subsequent studies still in progress, refined compositions for each phase have been calculated and prepared, yielding apparent monophase reference standards for the H, P, and Z matrix phases.[5])

The phases identified in these early specimens indicated that the carbonates had been completely broken down during the 775 to 800°C calcining step (the observed weight loss also agreed with the theoretical). Both the P and H phases were beginning to form at 775°C, before sintering shrinkage began. This is a particularly important point, since it is these phases that must be relied upon to incorporate, stabilize, and retain the most volatile radwaste species (e.g., oxides of cesium, molybdenum, and strontium) during subsequent sintering. It is evident from these data that stabilization begins well below their respective volatilization points. With the present rather coarse-grained ZrO_2 starting material, the Z phase was the last to form (none was observed by x-ray diffraction in firings at 800°C). This is not considered a significant detriment, since zirconolite is intended primarily as the host phase for actinides, which are not especially subject to loss by volatility.
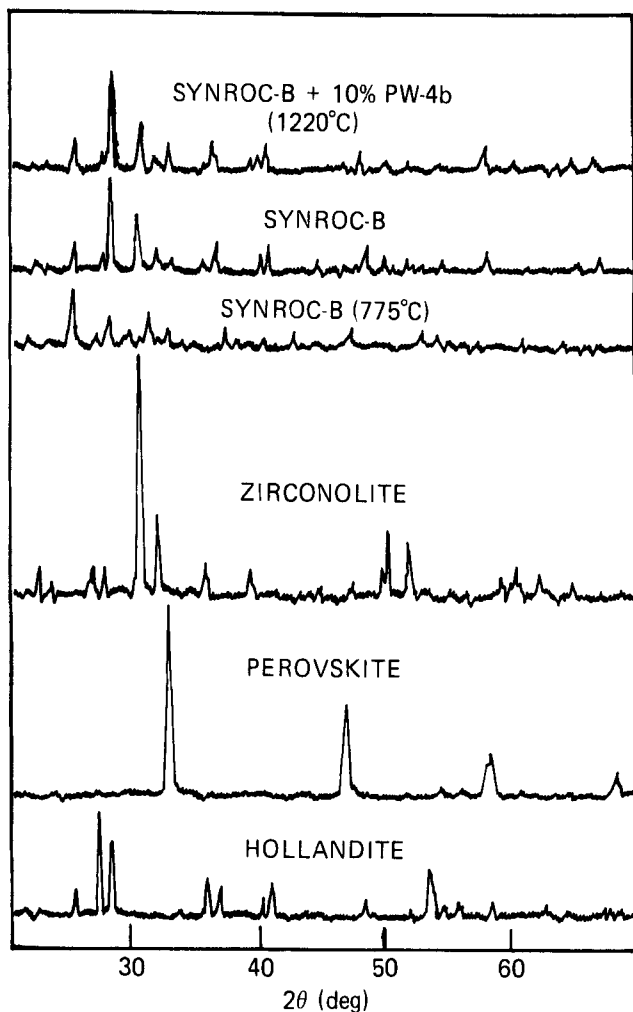
Fig. 1. X-ray diffraction patterns for sintered SYNROC-B ceramics with and without radwaste doping, and for the individual hollandite, perovskite, and zirconolite phases. (Dilatometer specimens at 1200°C unless otherwise noted; CuKα radiation at 35 kV, 20 mA).

No essential differences in the relative x-ray intensities or the number of phases formed were observed between the 1220°C firing and a 1420°C melt (not illustrated). These observations indicate that the subsolidus sintering conditions employed here result in essentially complete formation of the required phases (H, P, and Z) at temperatures as low as 1200 to 1220°C. They also indicate that at this relatively low sintering temperature these phases have been rendered as stable with respect to one another as at any higher temperature (including Ringwood's original hot pressing temperature, ≥1325°C) up to the melting point.

In the pure SYNROC-B material[1] and with the present nonoptimized composition and processing method, the three principal phases of the Ringwood Type B mineral assemblage were clearly observed as major constituents, but were also accompanied by calcium dititanate ($CaTi_2O_5$) and other minor phases, including some unreacted TiO_2. [The original Ringwood formulation[1] was found to contain excess TiO_2 and BaO, so in subsequent work still in progress,[5] compositional adjustments are being developed and tested, resulting in a Modified SYNROC B containing 10%

simulated radwaste, which, when fired, yields an x-ray pattern showing only the three principal phases (H, P, and Z)].

III. ADDITION OF RADWASTE

In all early experiments, up to 10 wt% simulated radwaste was added to the prepared SYNROC-B powder in an additional 6-h remilling step. After forming, compacts were heated in air to 775°C (below the volatility zone of the most volatile radwaste components) and held 8 h to remove all CO_2 from $CaCO_3$ and $BaCO_3$. For dilatometry experiments, prefired specimens were then encapsulated in platinum foil, along with a "getter" of yttrium metal foil to create a local reducing environment. Dilatometric readings were taken without difficulty through the thin foil envelope during firings to maximum temperature (typically 1200 to 1220°C) in an air atmosphere dilatometer described elsewhere.[4] With radwaste doping, phase formation at 775 and 1200°C was generally similar to that reported above for pure SYNROC-B; however, introduction of radwaste cations introduced more complexity in the diffraction patterns. Within the protective foil envelope in the initial dilatometer experiments, the measured weight loss was negligible, being no more than 0.001 g from a 1-g sample. In later studies, similar radwaste-containing specimens were successfully sintered, also without detectable weight loss, in an open tube furnace setting in a flowing, reducing gas mixture (argon, 4% H_2).

IV. RESULTANT DENSITY AND MICROSTRUCTURE

IV.A. Undoped SYNROC-B

After precalcining at 775°C, the microstructural appearance was very fine and rather uniform at 1000X but more complex at 9300X (Fig. 2a). The pure SYNROC-B reached a density of 4.02 g/cm^3 at 1220°C after 2 h and increased to 4.11 after 8 h (Fig. 2b). The approximate theoretical density of this composition was estimated to be 4.29 g/cm^3 (based on a rule of mixtures for the respective oxides), yielding a fractional density of ≥0.95 for the most dense specimen. The microstructure was fairly uniform, but showed a substantial number of pores somewhat larger than the average grain size (1 to 2 μm). Visual observation indicated porosity on the order of 5%; the sintered specimens did not absorb water.

IV.B. SYNROC-B + 10% Radwaste

After sintering, simulated radwaste-containing SYNROC material had a density ≤4.22 g/cm^3 (Fig. 2c). The porosity observed was considered to be consistent with the estimated 0.95 to 0.97 fractional density. The microstructure was distinctly different from the pure SYNROC-B, having smaller pores, with some grains showing a preferred growth direction. Pores were generally smaller than the grain size, and were well located at triple points and grain edges. Typical grain size was 1 to 3 μm. Material doped with 5% stimulated radwaste was not as dense as the 10% material, but had a very similar microstructure. These observations suggest that radwaste additions tend to improve, rather than hinder, the densification behavior, although they also tend to develop more heterogeneous microstructures.
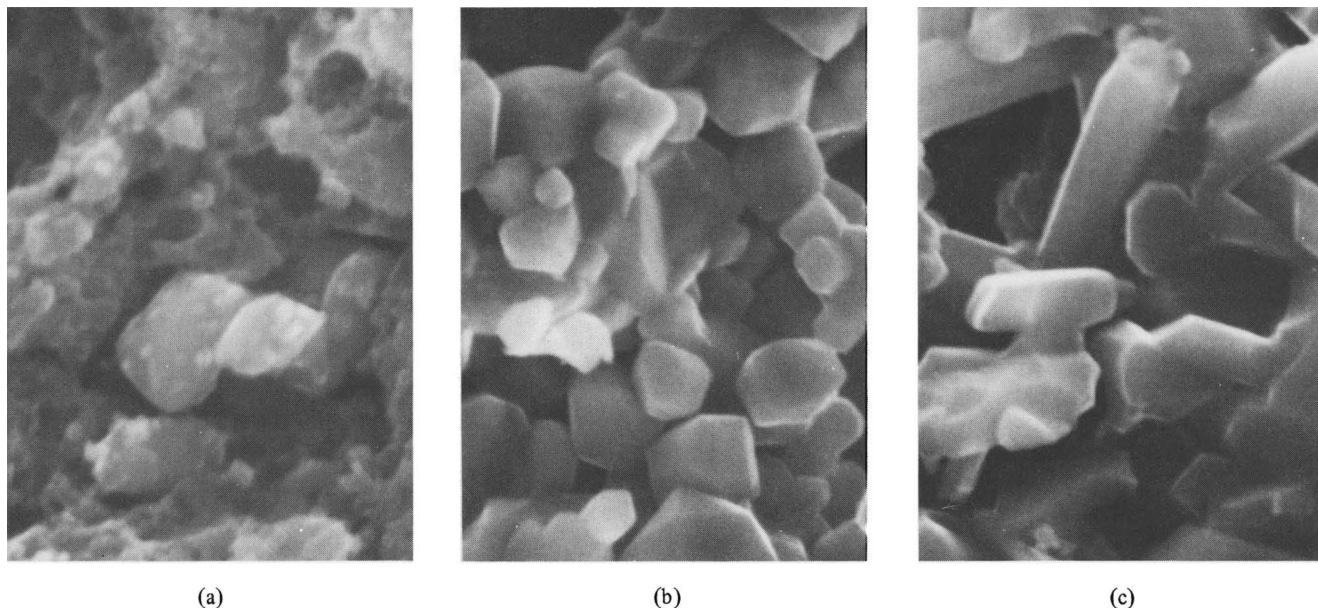
Fig. 2. Microstructures of sintered SYNROC-B ceramics, SEM, 9300X: (a) undoped, presintered at 775°C, 8 h in air; (b) undoped, sintered at 1200°C, 8 h in air; (c) doped with 10% simulated radwaste (PW-4b), sintered at 1220°C, 8 h, reducing atmosphere.

V. SUMMARY

The early studies reported here were carried out on a limited scale with available materials, facilities, and procedures, and with little opportunity to optimize any of the parameters involved. However, they appear to have demonstrated convincingly the feasibility of producing a technically dense, uniformly heterogeneous, fine-grained ceramic form of SYNROC-B containing 10% simulated radwaste. The material has been shown to respond well to more or less conventional ceramic powder processing methods, and to an appropriate three stage thermal treatment:

1. burnout of binder/lubricant at <450°C

2. calcining at 775 to 800°C to break down carbonates and to prereact the phases (H,P) that stabilize the most volatile radwaste species

3. solid-state sintering at ~1220°C in reducing atmosphere to densify the material and complete the formation of the three stabilizing phases (H, P, and Z).

Though systematic refinement and optimization of all individual steps and of whole process sequences remain to be done, and extensive characterization of the final sintered product will be required to assure that adequate stabilization of the various radwaste species has been achieved, these findings are considered sufficiently encouraging to warrant continued investigation of powder processing–subsolidus sintering as a realistic technological alternative to the hot pressing of SYNROC-B immobilized radwaste forms originally proposed by Ringwood et al.[1]

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