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COMPARISON OF CERAMIC WASTE FORMS PRODUCED BY HOT UNIAXIAL PRESSING AND BY COLD PRESSING AND SINTERING

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ABSTRACT

Synroc C waste form specimens prepared using the Australian-developed technology are uniaxially pressed in stainless steel bellows at 1200°C and 20MPa. This produces a material with high chemical and physical durability and with the radioactivity enclosed inside both the waste form and the bellows. An alternative method of producing the ceramic product is to use cold pressing of pellets followed by reactive sintering to provide densification and mineralization. Depending on the scale of waste form preparation required and on the activity level and nature of the waste streams, the cold press and sinter method may have advantages. To evaluate the effects of production method on waste form characteristics, especially resistance to dissolution or leaching of waste elements, we have prepared two simulated waste samples for evaluation. Both samples were prepared from liquid precursor materials (alkoxides, nitrates, and colloidal silica) and then doped with waste elements. The precursor material in each case corresponded to a basic phase assemblage of 60% zirconolite, 15% nepheline, 10% spinel, 10% perovskite, and 5% rutile. One sample was doped with 25% by weight of U; the other with 10% by weight each of U and Gd. Each sample was calcined at 750°C for 1 hr. in a 3.5% H₂ in N₂ atmosphere. Then one portion of each sample was hot pressed at temperatures ranging from 1120 to 1250°C and 20MPa pressure in steel bellows. A separate portion of each sample was formed into pellets, cold pressed, and sintered in various atmospheres at 1200°C to produce final products about 2/3 cm in diameter. Samples were then examined to determine density of the product, grain sizes of the phases, phase assemblage, and the location of the U and Gd in the final phases. Density data indicate that sintering gives good results provided that the samples are held at 200°C for long enough to allow trapped gases to escape.

INTRODUCTION

Many radioactive waste management options currently under consideration would generate waste streams that are high in actinide content. Examples of these waste streams are actinides that are separated from fission products during the reprocessing of commercial power reactor spent fuels, the fuel debris from reactor accidents, such as Chernobyl and Three Mile Island fuel residues, and plutonium from dismantled weapons. Two of these potential waste streams would consist of well characterized input streams to the immobilization process. The fuel residues from reactor accidents, however, would be rather poorly characterized and might present substantial challenges if the nature of the waste form required detailed chemical characterization of the waste prior to processing.

We performed a set of experiments to evaluate two factors relevant to actinide immobilization in a ceramic. First, what is the extent to which a single chemical composition with a given mineralogy can be chosen for a precursor material, maintaining the same phase assemblage, and allow waste to be added to the precursor without adjusting for the chemical substitutions caused by the waste elements to the basic mineralogy of the ceramic? Answering this question would allow an evaluation to be made of the relative costs of characterizing heterogeneous

waste streams versus adopting a lower waste loading that would produce predictable waste form quality without control of the waste input chemistry. We address this question through experiments involving doping of a particular ceramic formulation with uranium so that the final product is 25% by weight uranium, and with a mixture of U and Gd to produce a final ceramic that is 10% by weight in each of U and Gd.

The second factor that we evaluated was the method of densification and sintering. Synroc processing at ANSTO is done using hot uniaxial pressing of materials that have been placed in a steel bellows after calcination in a 3.5% H₂ in N₂ atmosphere at 750°C to remove water and nitrates. Other studies of Synroc preparation have investigated the use of cold pressing and sintering at ambient pressure. When oxide starting materials were prepared using extensive ball milling to ensure small particle size good densification and phase formation was found at temperatures only about 100°C higher than those used in hot pressing [1]. Cold pressing and sintering of small ceramic waste forms designed to immobilize the residues from treatment of mixed waste showed that use of powdered oxide starting materials provided sintered samples with 90% of theoretical density even without extensive ball milling [2].

The precursor materials used for Synroc C preparation at ANSTO are made using alkoxides of Ti, Zr, and Al, together with Ba and Ca hydroxides [3]. This process produces a very reactive, fine-grained powder that can be mixed with liquid or powder waste materials and yield a homogeneous distribution of the waste elements on the scale of micrometers after hot-pressing. For immobilization of fissionable actinides, it is very important to show that gross segregation of materials that might cause a criticality accident will not occur. The first step in this demonstration requires that intimate mixing be possible without elaborate requirements for mixing methods or precise gravimetric monitoring of the mixed powders. We judged that alkoxide precursor materials would give the best behavior in mixing processes. Since a previous attempt to sinter ceramics made with alkoxide precursors indicated that lower densities were achieved than with oxide materials [2], we decided to investigate this effect further by using materials prepared by alkoxide synthesis in our processing comparison. We have since learned that the failure to achieve high density with the alkoxide materials was due to the trapping of adsorbed gases and subsequent bloating effects during sintering.

EXPERIMENTAL PROCEDURES

The ceramic precursor materials were prepared using the normal ANSTO synthesis method of mixing alkoxides of Ti, Zr, and Al in ethanol and hydrolyzing these by adding an aqueous solution of the nitrates of Mg, Ca, and Na [3]. Ludox colloidal silica was added after the addition of the nitrates. The combination was mixed well and then the water was evaporated while mixing was continued. The target composition was a final product that prior to U or Gd addition that would produce 60% by weight of zirconolite (CaZrTi₂O₇), 15% nepheline (NaAlSiO₄), 10% spinel (MgAl₂O₄), 10% perovskite (CaTiO₃), and 5% rutile (TiO₂). The batch size was approximately 1200 g (equivalent oxide weight). A 400 g portion was doped with uranyl nitrate to produce a sample with final U concentration of 25 wt%; 400 g was doped with Gd and uranyl nitrates to produce a final sample containing 10 wt% each of Gd and U; and 400 g was shared between ANSTO and LLNL laboratories for experiments involving sintering. The two large samples doped with U and (Gd + U) were calcined in an atmosphere of N₂ + 3.5% H₂ at 750°C for 1 hr. Each sample was then mixed with 2% Ti metal to assure reducing conditions [3], poured into steel bellows of about 8 cm diameter and 8 cm height and pressed at 1120°C and 20 MPa

for 2 hours using a graphite susceptor and an induction furnace. Approximately 50 grams of each composition was also similarly prepared and pressed in bellows at 1170 and 1250°C to allow comparison of phase formation and densification.

Samples were prepared for sintering by adding the appropriate amount of nitrate solutions to small batches of the undoped precursor material described above. The doped materials were dried and calcined under conditions identical to those used for the hot-pressed samples. At LLNL, the samples were mixed with carbowax to act as a binder, pressed into pellets, and placed in a 3" tube furnace. A flow of Ar + 3.5% H₂ atmosphere was started through the furnace and then a programmed heating cycle was started. The temperature was ramped by 10 °C/min from ambient to 200°C and then held for 30 minutes to burn out the binder. Then the temperature was increased by 20 °C/min from 200 to 1200 °C, where it was held for 1 hour. The material doped with 25% U was pressed at 15,000 psi (103 MPa) prior to sintering. The material doped with Gd and U could not be formed into coherent pellets at low pressure. Pressing was eventually done at 40,000 psi (276 MPa) to produce acceptable pellets. Pressing at ANSTO was done using a hand press; no binder was used. Sintering was done at 1200°C in three different atmospheres - ambient air, nitrogen, and N₂ + 3.5% H₂ without a low temperature hold step.

RESULTS AND DISCUSSION

The undoped powders were pressed in a graphite die at 1150°C/20MPa and yielded an Archimedes density of 3.76 g/cm³, which is 96% of the theoretical density calculated based on the X-ray lattice parameters given in the JCPDS file. The 400 g samples pressed at 1120°C had Archimedes densities of 4.26 g/cm³ for the Gd + U sample and 4.06 for the U doped sample, with open porosities of 0.1 and 2.2% respectively. Both of these densities were lower than values expected based on the processing parameters normally used for preparation of Synroc samples; however, the x-ray diffraction data for these samples showed the expected phase assemblages, except that an additional UO₂-rich fluorite structured phase appeared in the U-doped sample. The lower than expected densities were no doubt due to the use of an insufficiently high pressing temperature. To investigate this possibility, a smaller sample of each composition (about 4 cm in diameter) was pressed at higher temperatures. The 1170°C samples gave densities of 4.42 g/cm³ for the Gd + U sample and 4.67 g/cm³ for the U-doped sample. The phases obtained by x-ray diffraction for these samples were the same as those found for the lower pressing temperature. The samples pressed at 1250°C had Archimedes densities of 4.52 g/cm³ for the Gd + U sample and 4.66 g/cm³ for the 25% U sample.

Back-scattered SEM images indicated the presence of approximately 10 to 20 micrometer-sized regions that had essentially uniform back-scattering intensity within themselves, apart from micrometer-sized intergrowths of the minor low-Z spinel and nepheline phases, and were bounded by thin, irregularly shaped regions (see Fig.1). Some porosity was clearly present also. The irregular boundaries of the 10-20 um-sized zones suggest that they are not fully-developed zirconolite grains containing intergrowths of other phases, but rather that they are relict structures of agglomerates, which were originally present in the calcine. It is believed that hot pressing has induced a small amount of melting of a metastable glassy phase and that this has flowed into the spaces between the agglomerates to yield the observed dark boundaries between the zirconolite-rich regions. The intensity contrast between the different zirconolite-rich zones is probably due to some variation in the concentrations of U and Gd, which may have occurred during the late stages of evaporative drying in

the original mixtures. This has been observed in similar microstructures formed in the pellets sintered at 1200°C in the Ar/H₂ atmosphere (see below). The intrinsic size of the zirconolite grains is probably sub-micron. The U-doped samples showed similar agglomerate structures, but with the addition of 0.5 μm UO₂-rich grains.

At LLNL, twelve pellets of U-doped calcined precursor materials were pressed at 15,000 psi and sintered at 1200°C in Ar + 3.5% H₂. The green densities averaged 2.06 g/cm³ with a standard deviation of 0.04 g/cm³. The sintered bulk density, which includes both open and closed porosity, averaged 3.26 \pm 0.09 g/cm³, while the Archimedes density, which includes only closed porosity, was 4.28 \pm 0.08 g/cm³. This is intermediate between the densities found for hot pressing at 1120 and 1170°C. Two samples were prepared under nominally identical conditions at ANSTO and resulted in bulk densities of 2.82 g/cm³ and Archimedes density of 3.22 g/cm³. The theoretical density for this composition must be at least the density of 4.67 g/cm³ obtained by hot pressing at 1170°C. It is not possible to calculate an accurate theoretical density for these samples, since the exact proportions of phases are not known. The ratio of the Archimedes density of the LLNL sintered samples to the hot pressed density is 91.6%, while that for the ANSTO samples is 69%. Experience with alkoxide starting materials for a somewhat different phase assemblage sintered in air by heating from ambient temperature to 1150°C without a low temperature hold step gave samples with about 75% of theoretical density [2]. It appears that the combination of use of a binder together with a hold step to burn the binder out along with adsorbed air and moisture gives the best result for densification by sintering for alkoxide precursor material.

Table 1: Densities of samples sintered in hydrogen-containing atmospheres and of hot pressed samples in g/cm³.

<u>Preparation method</u>	<u>25% U samples</u>	<u>10% Gd + 10% U samples</u>
LLNL, bulk density	3.26	3.57
Archimedes	4.28	4.15
ANSTO, bulk density	2.82	3.74
Archimedes	3.22	3.84
Hot-pressed 1120°C	4.06	4.26
1170°C	4.67	4.42
1250°C	4.66	4.52

Densities for the samples doped with Gd + U and sintered in H₂-containing atmospheres are given in Table 1, together with those for the U doped samples. For the Gd + U doped samples, the difference in density between samples hot pressed at 1120 and 1170°C is less than that for U-doped samples, perhaps due to the absence of a separate U oxide phase. The bulk densities for the LLNL and ANSTO sintered Gd + U samples are similar, but the LLNL samples achieved a higher Archimedes density (93.9% of the highest hot pressed density). The green density for the LLNL samples was 2.14 \pm 0.01 g/cm³ for a set of seven pellets. Samples sintered in air and in nitrogen have similar appearances as seen in scanning electron microscope

images to those sintered in hydrogen-nitrogen mixed gas. X-ray diffraction data for those samples also show the same phases and no evidence for a segregated phase containing U. This is not surprising, since Vance and Agrawal [4] showed that U would enter the Zr site in zirconolite for air-fired samples.

The phase assemblage obtained for samples containing 25% U varied with the sintering atmosphere. When hydrogen-containing atmosphere was used, a UO_2 -rich fluorite structure phase was seen as a separate phase, as was observed for the hot-pressed samples. We had originally thought that ZrO_2 might segregate and that the U would be entirely incorporated into the zirconolite in the Zr site under reducing conditions, but no evidence for ZrO_2 was found in any of the x-ray data. Samples sintered in nitrogen did not show UO_2 , but do show tazheranite $(\text{Zr,Ca,Ti})\text{O}_2$ in the x-ray data. The sample sintered in air showed only zirconolite and calcium-uranium-oxide ($\text{Ca}_2\text{U}_3\text{O}_{11}$) as positively identified peaks in the x-ray data, with the $\text{Ca}_2\text{U}_3\text{O}_{11}$ formed preferentially at the pellet surface. Because of the variation in phase composition for these samples and the uncertainties in the abundance of the phases, it is not meaningful to compare densities of samples to each other, since they would all have different theoretical densities.

The samples prepared at LLNL were analyzed using wave length dispersive electron microprobe methods. Two micrographs from one of the Gd + U pellets are shown in Figure 2. Two distinct zirconium-rich phases were identified, Phase A and Phase B, as well as a high-atomic number multiphase aggregate. Representative analyses for Phases A and B are given in Table 2. Both of these phases contain high amounts of Gd and U, but the Gd/U ratio is different for the two phases. The morphology of the phases suggests exsolution or entrapment of minor phases in the zirconium-rich phase. Since Si is not normally incorporated into zirconolite, we recalculated the compositions normalized to 21 oxygen atoms after subtraction of enough nepheline component to reduce Si to zero. The occupation of the Ca site was still too high for zirconolite, so we further removed a spinel component from the data by reducing Mg to zero and removing enough Al to form spinel. Recalculation to cations per 21 oxygens gave 12.55 cations per 21 oxygens for Phase B (first column) as compared to a theoretical value of 12 cations for zirconolite. This indicates that there is still some low-cation charge phase that has not been accounted for. The site occupancy for Phase B indicated from the recalculated analysis is $\text{Ca}(\text{Zr,Gd,U})(\text{Ti,Al})_2\text{O}_7$. A similar recalculation exercise for Phase A indicated that Gd was present on both the Ca and the U site, in roughly equal amounts.

These data are in qualitative agreement with ANSTO results on doping zirconolite with individual rare earths and actinides [5]. The U^{4+} and the heavier rare earths can be readily accommodated in either the Ca or Zr sites, given the existence of suitable charge compensators, while the light rare earths have a strong preference for the Ca site.

Chemical calculations have been carried out on our chosen phase assemblage, based on our accumulated knowledge of the modes of entry of Gd and U into zirconolite and perovskite. The calculated solid solubility limit correctly predicted that the 10 wt % each of Gd and U can be incorporated, but also showed that to incorporate 25 wt% U (in the absence of forming ZrO_2), more Ca and Ti need to be added to the basic formulation.

CONCLUSIONS

Samples of a Synroc-type waste form with 60% zirconolite have been successfully prepared by both hot-pressing and by sintering. The combination of use of a binder together with a hold step to burn the binder out along with adsorbed air and moisture gives the best result for densification by sintering for alkoxide precursor material.

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Table 2: Electron probe data for Gd + U doped sample sintered in Ar + 3.5% H₂ at 1200°C.

Phase	B	B	Hi-Z ¹	A	A
ZrO ₂	14.23	14.22	18.13	15.26	15.57
TiO ₂	31.66	31.05	35.68	34.52	33.43
SiO ₂	1.19	1.14	0.51	1.39	0.76
Al ₂ O ₃	14.04	13.76	9.54	7.96	8.75
MgO	4.41	4.52	2.56	2.5	3.35
CaO	12.28	11.85	11.36	12.24	11.0
Na ₂ O	1.06	1.00	0.71	1.1	0.78
Gd ₂ O ₃	10.94	10.72	9.64	15.82	16.26
UO ₂	9.54	8.80	11.83	9.38	10.53
Total	99.37	97.06	99.95	100.17	100.43

Cations normalized to 21 oxygens

Zr	1.22	1.24	1.60	1.38	1.41
Ti	4.19	4.19	4.86	4.80	4.68
Si	0.21	0.20	0.09	0.26	0.14
Al	2.92	2.92	2.04	1.73	1.92
Mg	1.16	1.21	0.69	0.69	0.93
Ca	2.32	2.28	2.20	2.42	2.19
Na	0.36	0.35	0.25	0.40	0.28
Gd	0.64	0.64	0.58	0.97	1.00
U ⁴⁺	0.37	0.35	0.48	0.39	0.44
Total	13.39	13.38	12.79	13.04	12.99

¹Multiphase aggregate.

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10% GL + 10% LL
1170°C



Fig. 1 Back-scattered SEM image of 10% GL + 10% LL sample pressed at 1170°C.

Figure 2

Sample 7 - U- and Gd-bearing

Hi-Z aggregate

