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SINTERING OF SYNROC D

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ABSTRACT

Sintering has been investigated as a method for the mineralization and densification of high level nuclear defense waste powder. Studies have been conducted on Synroc D composite powder LS04. Optimal densification has been found to be highly dependent on the characteristics of the starting material. Powder subjected to milling, which was believed to reduce the level of agglomeration and possibly particle size, was found to densify better than powder not subjected to this milling. Densities of greater than 95% of theoretical could be achieved for samples sintered at 1150 to 1200°C. Mineralogy was found to be as expected for Synroc D for samples sintered in a CO₂/CO atmosphere where the Fe⁺²/Fe⁺³ ratio was maintained at 1.0 to 5.75. In a more oxidizing, pure CO₂ atmosphere a new phase, not previously identified in Synroc D, was found.

INTRODUCTION

Synroc, an acronym for synthetic rocks, is a ceramic material developed for the long term immobilization of high level nuclear wastes. The Synroc concept was introduced by A. E. Ringwood.¹ He proposed a waste disposal system consisting of a man-made analogue of natural minerals. These minerals were known to have successfully retained naturally occurring radioactive elements over geologic time (20-200 million years).² The mineral assemblage chosen by Ringwood was based on titanate species which are known to have an extremely low solubility in ground water environments. The radioactive waste elements are incorporated into these minerals as dilute solid solutions.

The Synroc waste form has major advantages over borosilicate glass. The borosilicate glass can devitrify readily when subjected to water at elevated temperature and pressure to form crystalline phases, which are less stable with regard to hydrothermal leaching.¹ This would make the glass waste form susceptible to leaching in its underground burial site. In Synroc the radioactive elements are actually contained in the crystal structure of mineral phases known to be highly resistant to hydrothermal alteration in geological environments.

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Synroc D Composition

Synroc D has been developed to immobilize high level nuclear wastes derived from defense related activities. Some of these wastes are now stored in tanks at the Savannah River Plant near Aiken, South Carolina.³ The waste is chemically diverse. A composite composition, representing the average for the total inventory at Savannah River, has been used to formulate Synroc D.

Synroc D is composed of the coexisting mineral phases zirconolite, perovskite, nepheline, and spinel.⁴⁻⁷ Zirconolite, $(\text{CaZrTi}_2\text{O}_7)$, and perovskite, (CaTiO_3) are titanates of very low solubility when compared to glass. They are capable of incorporating radionuclides in their crystal structures at low concentration. Uranium replaces Zr in zirconolite, while the actinides and rare earth elements are partitioned between zirconolite and perovskite.^{3, 5-7} Strontium is primarily contained in perovskite.^{3, 5-7} Nepheline $(\text{NaAlSi}_3\text{O}_8)$ is a silicate phase that forms due to the presence of Na and Si in the defense waste. The Cs present in the radwaste partitions strongly into the nepheline phase. Other forms of Synroc, developed for commercial rather than defense radwaste, substitute hollandite $(\text{BaAl}_2\text{Ti}_6\text{O}_{16})$ for nepheline as the Cs host. Hollandite, a titanate, is more leach-resistant than nepheline, a silicate.⁷ A spinel mineral phase, $(\text{R}^{2+}\text{O} \cdot \text{R}_2^{3+}\text{O}_3)$ containing no radionuclides forms from the aluminum and transition metals present in the waste.⁷

Synroc Preparation

Several methods for the preparation of Synroc have been proposed. These include isostatic hot pressing, uniaxial hot pressing, and cold pressing followed by sintering.⁴ Sintering is the method that is investigated in this work. Sintering is well established in ceramic processing and therefore is considered to be the most reliable and economical method of those proposed. A Synroc production facility would have to be operated remotely due to the hazards associated with radioactive materials. Thus, the equipment used would need to be reliable and easy to maintain. These factors give sintering a distinct advantage in the consideration of large-scale Synroc production.

Sintering

Sintering is a method used in ceramics and metallurgy for the densification of a compacted powdered material. Sintering results in shrinkage of the compact and reduction of its porosity. In subsolidus sintering the material is held at a temperature below the melting point while densification takes place. The effects of different variables related to proposed sintering mechanisms are best understood for simple single phase systems. Synroc, however, is a complex multiphase system in which sintering can be expected to be a more complicated process.

For single phase systems models have been developed for various mechanisms of material transfer during sintering such as evaporation and condensation, viscous flow, plastic deformation, surface diffusion, and bulk or lattice diffusion.⁸ Only mechanisms which lead to a decrease in the distance between particle centers leads to densification. The driving force of sintering is the lowering of the surface free energy that occurs when the surface area is reduced. A summary of sintering equations for various bulk diffusion models has been given by Coble and Burke.⁹

A simple model for the bulk diffusion process can be developed for the sintering together of two single crystal spheres.¹⁰ This is a solid state process in which material transport takes place from the grain boundary at the contact area between spheres to the surface of curvature at the "neck" as shown in Figure 1. An equation for the bulk diffusion mechanism can be derived by applying the Kelvin equation, which gives the effect of surface curvature on the molar free energy of a substance.¹¹ In the bulk diffusion process lattice vacancies diffuse away from the surface of the neck, an area of high negative curvature and high vacancy concentration. The vacancies diffuse towards the nearly planar grain boundary between the two spheres to produce a shrinkage such that the centers of the spheres move together.

The equation for the linear fractional shrinkage for this model can be given as:¹⁰

$$\frac{\Delta L}{L_0} = \left(\frac{K'}{r^3} \right)^{2/5} t^{2/5} \quad (1)$$

where: L_0 is the original distance between sphere centers,
 ΔL is the change in that distance,
 r is the radius of the spheres,
 t is time,
and K' is a temperature dependent proportionality constant.

The constant K' is dependent on such parameters as temperature, the grain boundary energy, the self diffusion coefficient and the atomic volume of a diffusing entity.

As shown in equation 1, the sintering rate steadily decreases with time, so that there is a limiting value for the sintering time beyond which densification does not greatly increase. The diffusion coefficient is affected by composition and by temperature. The sintering rate is roughly inversely proportional to particle size.⁸ Particle size distribution is also important. If the particles form agglomerates the agglomerates may sinter together rapidly leaving pore space within the agglomerates. Milling the powder to break up the agglomerates may substantially increase the densification and sintering rate.⁸

In this work, sintering of Synroc D will be studied. The purpose of this study is to determine conditions under which Synroc D can be sintered to >95% of theoretical density (T.D.) below the solidus temperature and to study the effects of agglomeration on sintering behavior.

Preliminary work on Synroc D has been done by Holt.¹² In his work with conventionally spray dried Synroc D powders sintered densities of above 95% theoretical could not be achieved at subsolidus temperatures. At temperatures

of 1150°C and above, there was evidence of a glassy phase formation. Differential thermal analysis data for Synroc D is shown in Figure 2. The DTA data indicates that a phase change occurs at about 1180°C. This phase change could represent the onset of glassy phase formation.

Previous work on sintering of Synroc for commercial waste has also been done by H. Palmour III et al., at North Carolina State University.^{13,14} His group studied subsolidus sintering of a Synroc waste form which differs mineralogically from Synroc D.

METHODS

Preparation of Synroc D Powder for Sintering

A schematic outline of the procedure used to study the sintering behavior of Synroc D is given in Figure 3. The Synroc D LS04 Powder used in these experiments has a composition as given in Table 1.⁵ It is a duplicate of S-29 reference powder used in previous studies.⁶ It consists of a composite sludge containing depleted U²³⁸ developed to simulate Savannah River Plant wastes. Ingredients necessary for the formation of Synroc D are added to this simulated sludge. The composite sludge is made up using soluble nitrates or hydroxides of the elements, which simulates the characteristics of the material in the Savannah River Plant waste disposal tanks. The Synroc additives are mixed into the sludge. In the case of TiO₂ a pigment grade oxide was used.⁶ The SiO₂ was added as colloidal silicate, Zr as ZrO₂, and Ca as the nitrate salt.⁶ The components of the composite sludge and the Synroc additives are mixed as an aqueous slurry, and then spray dried to form a homogeneous powder.

After spray drying, the powder was first rotary calcined in an argon atmosphere at 600°C for 18 hours.¹⁵ The calcination step decomposes the hydroxide and nitrate salts to metal oxides. The material was then rotary redox calcined in a CO₂/CO atmosphere at 600°C for 1 hour.¹⁵ The CO₂/CO atmosphere was maintained at a ratio of 2.9/1.0. This provided an oxygen partial pressure of about 10⁻²⁴ atm which under equilibrium conditions should provide an Fe⁺²/Fe⁺³

ratio in the magnetite range.¹⁶ For the composite Synroc D composition an iron ratio in the magnetite range promotes formation of a spinel phase in which a minimum amount of TiO_2 is consumed.⁶

Grinding

After the redox calcination step the LS04 Synroc D powder was split in half. Half the powder was subjected to grinding in a vibro energy mill in an attempt to break up any agglomerates that might exist in the spray dried powder. Agglomeration causes void spaces which adversely affect the densification behavior during subsolidus sintering. A Sweco Model M 18-5 vibroenergy mill was used to grind the powder. The powder was vibromilled wet, in isopropyl alcohol, for 48 hours using Al_2O_3 grinding cylinders. Earlier experiments have shown that little or no Al_2O_3 contamination occurs during grinding. Both the milled and unmilled powders were carried separately through the remaining steps of the study shown in Figure 3.

Binder and Lubricant Addition

An organic binder, Carbox 4000, (Union Carbide, Danbury, CT) was added to the milled and nonmilled powders. The binder was added to assure sample integrity and assist in densification during the cold pressing step. An amount of Carbowax 4000 corresponding to 2.5 wt% of the Synroc samples was first dissolved in isopropyl alcohol. The Synroc powders were added to the solution, which formed a wet slurry. The isopropyl alcohol was then allowed to evaporate while stirring to distribute the binder uniformly. A lubricant, isosteric acid (No. 871, Emery Industries, Cincinnati, Ohio) was also added (2.5 wt%) to the powders. The lubricant aids in forming of the green pellets and reduces die wall friction. The lubricant was added using an automatic alumina mortar and pestal to assure uniform distribution. The selection of binder and lubricant was based on information from studies at North Carolina State University.^{13,14}

Cold Pressing

The samples were cold pressed using an Enerpac Model RC251 uniaxial press and a half inch diameter carbide lined stainless steel die. Sample size, (1.3 g) was selected to yield a length to diameter ratio of about 0.5 for the pressed pellet. Samples were pressed at 2000 psi and held at that pressure for five minutes.

Binder Burnout

Removal of the binder and lubricant in previous work^(13,14) was done by slow heating in air to 400°C over time periods up to 24 hours. In this work it was found that when the binder burnout was done in air, the samples turned reddish brown, indicating that iron oxidation had taken place. The samples were held in air at 400°C for a minimum of four hours and as long as 16 hours with the same results. Because oxidation is undesirable, an argon atmosphere was also tried to maintain redox control of the sample. The binder and lubricant were burned out of the sample pellets by slow heating (5°/minute) to 400°C. Thermogravimetric analysis of both binder and lubricant under air and argon atmosphere was done to determine the effectiveness of the change in atmosphere for removal of the organic material.

Sintering

Samples were sintered using a Lindberg Model 54459 furnace (Figure 4) which employs a Model 59545A three-zone temperature controller capable of maintaining a 12 inch constant temperature region. The furnace was equipped with a 2.5 in O.D. alumina tube and fittings so that a controlled atmosphere could be provided. The samples rested on an alumina boat that could be inserted into or withdrawn from the furnace by means of an alumina push rod. Up to 12 samples could be sintered at a time. Sintering temperature was determined by a chromel/alumel thermocouple which was contained in the push rod and the tip of which rested directly below the sample boat. Samples were brought up to temperature at a rate of 5°C/minute and sintered for one to five

hours at 1100°C, 1150°C, and 1200°C. Heating rates were controlled manually. Cooling rates, after sintering, were also 5°C/minute down to a temperature (800°C) where the furnace power could be shut off and a cooling rate of 5°C/minute or less maintained. Sintering temperatures above and below the solidus temperature were selected based on the basis of the differential thermal analysis data shown in Figure 2 and the assumption that the solidus temperature is about 1180°C.

Atmosphere Control During Sintering

To ensure the correct mineralogy and the proper utilization of TiO_2 in the finished product, the $\text{Fe}^{+2}/\text{Fe}^{+3}$ ratio was carefully controlled during sintering. This was accomplished by maintaining a specified oxygen fugacity through the control of CO_2/CO ratios in the gas atmosphere flowing over the samples. The oxygen fugacity required for a given $\text{Fe}^{+2}/\text{Fe}^{+3}$ ratio and that produced by a given CO_2/CO ratio are both functions of temperature. For the temperature range in this study (1100°C to 1200°C), a CO_2/CO gas ratio at 10:1 maintained the desired $\text{Fe}^{+2}/\text{Fe}^{+3}$ ratio.¹⁶ During sintering, the total gas flow rate was on the order of 100 cc/min. Some sintering studies were done using a pure CO_2 atmosphere to determine the effects of a more oxidizing environment.

DISCUSSION OF RESULTS

Starting Materials

The physical properties of both the vibromilled and nonmilled powders (before binder and lubricant addition) were investigated. Results for density, surface area, and particle size are shown in Table 2. Density was determined using a helium gas comparison pycnometer. The surface area of the powder materials was determined by absorption of nitrogen and calculated using the BET equation for multilayered adsorption of gases on solid surfaces. The particle size range was determined by image analysis of particle diameter from the projected area assuming an equivalent sphere. This method could not be used for the vibromilled powder as the particle size was below detection limits ($<1\mu$).

SEM photomicrographs of the milled and nonmilled powder are shown in Figures 5 and 6. The nonmilled particles are spherical in nature. The spheres appear to be a collection of agglomerated smaller particles. The vibromilled powder is much finer grained and seems to be composed of fragments of the agglomerated spheres. Each fragment consists of a few of the smaller particles agglomerated together.

Binder Burnout

Thermogravimetric analysis studies of binder burnout were done using 50 mg samples of the binder, Carbowax 4000. Tests were done at 5°C/minute up to a maximum temperature of 400°C. Results indicate that in an air atmosphere, the binder burns out from 180°C to 200°C. In an argon atmosphere the binder leaves at 320°C to 360°C. Weight loss appears to be rapid and complete although a very fine coating of sooty residue is left on the pan in both cases. TGA studies of the lubricant, isosteric acid, in argon indicate that it is vaporized at 180°C to 200°C. Sintering experiments were run employing pellets that had been exposed to either an air or argon atmosphere during burnout.

Sintering

A listing of the conditions for 13 sintering experiments are shown in Table 3. Bulk density measurements after sintering are also given in Table 3. Volumes for the bulk density calculations were measured with a micrometer, and theoretical Synroc D density was taken as 4.0 g/cc. The results show there is a pronounced improvement in densification for pellets formed from vibromilled powder as compared to nonmilled powder at temperatures of 1150°C or less. The average vibromilled powder is 96% of theoretical at 1150°C while the average non-milled powder is only 84% of theoretical. There is a sharp drop in densification achieved at 1100°C as compared to 1150°C for both types of powder. Increasing sintering time from two to five hours did not significantly improve density at 1100°C for both powders. At 1200°C both powder forms sinter equally well. Furthermore, sinterability at 1200°C is not

degraded by the more oxidizing, pure CO_2 atmosphere. It does not appear that the atmosphere used for binder significantly affects the final sintered density.

Samples in experiments LS04SR7A and LS04SR8A sintered at 1200°C had some pellets stuck to the alumina boat after sintering, indicating that partial melting had taken place. The sintering temperature for these samples was exceeded temporarily and reached 1215°C for a period of less than five minutes.

Optical micrographs at a magnification of 1000x are given in Figures 7-9 for experiments LS04SR5C, LS04SR7A, and LS04SR9A. The sample from experiment LS04SR5C (Fig. 7) sintered at 1150°C appears to be extremely fine-grained, LS04SR7A (Fig. 8) sintered at 1200°C is much coarser, and LS04SR9A (Fig. 9) sintered at 1200°C in pure CO_2 shows some evidence of needle-like crystals not seen in the other samples.

The $\text{Fe}^{+2}/\text{Fe}^{+3}$ ratio after sintering was measured for samples from two experiments as shown in Table 4. The sample from experiment LS04SR5C had an iron ratio of 5.75. This is in the wüstite magnetite two-phase range. Samples in this experiment had binder burnout under Ar and were sintered at 1150°C in a 10:1 CO_2/CO atmosphere. The other sample was from experiment LS04SR10A. This sample had an iron ratio of 0.70. The more oxidized value was expected as this sample was sintered in pure CO_2 .

X-ray powder diffraction analysis for experiments LS04SR5C and LS04SR9A are given in Figures 10 and 11. The LS04SR5C sample represents a typical Synroc D pattern. It was sintered at 1150°C under a 10:1 CO_2/CO mixture. The LS04SR9A experiment was run in pure CO_2 . This LS04SR9A sample has a major amount of a new mineral phase.¹⁷ X-ray crystallographic data for this phase, as seen in the LS04SR9A sample, is given in Table 5. This phase appears to be very similar to that seen by Morgan and Ryerson in a Synroc D sample with most of the iron in the trivalent state.¹⁸ The phase they saw was believed to be similar to murataite. X-ray crystallographic data for their phase is given in Appendix A. The data given in Table 5 is very similar to the major lines of the data in Appendix A.

Leaching Studies

A crushed sample from experiment LS04SR5C was submitted for leaching studies. Results are shown in Table 6, and compared with the leaching behavior of a LS04 Synroc D reference sample, hot pressed at 1150°C.¹⁹ A MCC-3 type test was used.⁶ This is a high temperature (150°C) solubility test on crushed samples, using deionized water as the leachant. One gram crushed samples were sieved to a particle size range of 150-300 μ m and rinsed in isopropyl alcohol. Cesium concentrations before and after leaching were determined by x-ray fluorescence.

The results show a lower value for initial cesium content in the sintered as compared with the hot pressed sample which reflects in part some loss of cesium due to volatilization during sintering. Leaching losses were comparable for both samples.

CONCLUSIONS

Sintering has been demonstrated to be a successful method for the mineralization and densification of Synroc D powder. In this work, it has been shown that densities of greater than 95% of theoretical can be obtained by sintering at 1150 to 1200°C. The x-ray diffraction patterns demonstrate that good Synroc mineralogy can be achieved. At high oxidation states a new Synroc phase was formed. Leaching studies have shown that this sintered Synroc D is comparable in leach resistance to hot pressed material.

It has been clearly shown that the vibromilled powder yields much higher sintered densities than the nonmilled powder at temperatures of 1150°C and below. The agglomerated nonmilled powder achieved densities after sintering of no better than 85% of theoretical at 1150°C. Thus, it seems apparent that for production scale fabrication of Synroc D by sintering it would be necessary to control the characteristics of the starting material, such as particle size and particle distribution, and particularly the level of agglomeration. For a spray dried powder, it would appear that a grinding step would be required if sintering were employed as the densification method.

Densification was found to drop off rapidly with temperature. This implies that furnace temperature would have to be closely controlled. Atmosphere during binder burnout appeared to be not crucial. The binder burnout step could be combined with the preheating phase of sintering. It may be possible to reduce cesium losses during processing by optimizing the heating rate and reducing the total amount of time spent below the sintering temperature. Sintering time could also be optimized. Based on the studies at 1100°C additional sintering time did not greatly improve densification.

A fairly wide variation in the $\text{Fe}^{+2}/\text{Fe}^{+3}$ ratio, from 5.75 to 0.70 yielded highly densified (> 95% T.D.) sintered pellets. Further investigation into leaching and other properties of the new phase (believed to be a pyrochlore) formed under oxidizing conditions, would need to be done if sintering were to be done in an oxidizing atmosphere.

If starting powder characteristics can be controlled, sintering would appear to be a viable alternative to hot pressing or isostatic hot pressing as a Synroc fabrication technique.

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Table 1

Nominal oxide composition of Synroc D Sample LS04 containing simulated
SRP composite sludge*

Component oxide of salt	SRP Composite sludge composition (wt%)	Synroc additives (wt%)	Total (wt%)
Fe_2O_3	23.8	-	23.8
Al_2O_3	18.6	-	18.6
MnO_2	7.4	-	7.4
U_3O_8	2.1	-	2.1
CaO	1.8	5.3	7.1
NiO	3.0	-	3.0
SiO_2	0.6	6.6	7.2
Na_2O	3.3	-	3.3
Na_2SO_4	0.6	-	0.6
Cs_2O	0.25	-	0.2
SrO	0.25	-	0.25
Ce_2O_3	0.50	-	0.50
Nd_2O_3	0.50	-	0.50
TiO_2	-	18.8	18.8
ZrO_2	-	6.6	6.6
Total wt%	62.7	37.3	100.0

* From reference 5

Table 2
Physical Properties of Synroc LS04 Powder

	Vibromilled	Not Milled
Density	3.62 g/cc	3.98 g/cc
Surface Area	19.660 m ² /g	17.774 g.m/g
Particle Size Range	<1μ	90 %wt <30 μ*
		50 %wt <15 μ
		10 %wt <8 μ

* Numerically 50% of all particles were <5 μm

Table 3
Sintering Experiments

Experiment	Binder Burnout	Atmos.	Temp. °C	Time Hrs.	Powder Milling	Sintered Densities (Percent of Theoretical Density)	
						Argon Binder Burnout	Air Binder Burnout
LS04SR1A	Air/Ar*	CO ₂ /CO	1100	2	Vibromilled	77	71
LS04SR2A	Air/Ar*	CO ₂ /CO	1100	2	Not milled	58	66
LS04SR3A	Ar	CO ₂ /CO	1100	5	Vibromilled	80	
LS04SR4A	Ar	CO ₂ /CO	1100	5	Not milled	59	
LS04SR5A	Air/Ar*	CO ₂ /CO	1150	2	Vibromilled	98	96
LS04SR5B	Air/Ar*	CO ₂ /CO	1150	2	Vibromilled	95	94
LS04SR5C	Ar	CO ₂ /CO	1150	2	Vibromilled	96	
LS04SR6A	Air/Ar*	CO ₂ /CO	1150	2	Not milled	88	87
LS04SR6B	Air/Ar*	CO ₂ /CC	1150	2	Not milled	81	81
LS04SR7A	Air/Ar*	CO ₂ /CO	1200	1	Vibromilled	96	94
LS04SR8A	Air/Ar*	CO ₂ /CO	1200	1	Not milled	95	93
LS04SR9A	Air/Ar*	CO ₂	1200	2	Vibromilled	94	92
LS04SR10A	Air/Ar*	CO ₂	1200	2	Not milled	93	88

* 50% of pellets in these experiments done each way (pure Ar or in air).

Table 4
Iron Ratios

Samples	Fe ⁺² /Fe ⁺³
After Redox Calcination	1.34
Sintering at 1150° CO ₂ /CO 10:1 (LS04SR5C)	5.75
Sintering at 1200°C pure CO ₂ (LS04SR10A)	0.70

Table 5
X-ray Diffraction Data for New Mineral Phase
in Sample from Experiment LS04SR9A

D _{obs}	HKL	I/I ₀
2.812	111	100
2.435	200	19
1.719	220	37
1.465	311	52 *
1.404	222	5

* Overlapped with line from spinel phase, which affects the intensity comparison for this peak.

Table 6
Leach Test Results for Cs

SAMPLE NO.	INITIAL Cs CONCENTRATION	WEIGHT PERCENT Cs LOST		
		1st day	2nd day	3rd day
LS04SR5C*	0.13%	1.1	0.8	-
LS04HP3A**	0.20%	1.62	0.88	0.74

* Vibromilled, sintered at 1150°C/2hr, CO₂/CO 10:1

** Hot pressed 1150°C in graphite¹⁹

Figure 1 Simple model for the sintering of two single crystal spheres (after Burke¹⁰).

Figure 2 Synroc D Calcined Powder - Differential Thermal Analysis (DTA) in Argon, Heating Rate = 20°C/min.

Figure 3

Sintering Experiments

Figure 4. Furnace Used for Sintering

Figure 5a

SEM photomicrograph of the normilled
Synroc D L804 Redox 5 powder
Mag. = 1000X

Figure 5b

SEM photomicrograph of the normilled
Synroc D L804 Redox 5 powder
Mag. = 5000X

Figure 6a

SEM photomicrograph of the vibromilled
Synroc D LS04 Redox 5 powder
Mag. = 5000X

Figure 6b

SEM photomicrograph of the vibromilled
Synroc D LS04 Redox 5 powder
Mag. = 20,000X

Figure 7

Sample LS04SR5C
Sintered in CO₂/CO
1150°
Met. No. 2844
Mag. = 1000X

Figure 8

Sample LS04SR7A
Sintered in CO₂/CO
at 1200°C
Met. No. 2855
Mag. = 1000X

Figure 9

Sample LS04SR9A
Sintered in CO₂
at 1200°C
Met. No. 2854
Mag. = 1000X

1727 3-11-82 DIF SAM 42, 43, 46 & 51 COMBINED
 INITIAL 2THETA= 10.000 DELTA 2THETA= 0.040 TIME INTERVAL= 4.00SEC
 ISM= 9 IBKG= 3 1 TGKAP= TGDSP-CU NDE= 9 SENS= 0.1 NUM= 1 IPF= 5

Figure 10 X-ray crystallographic data for a sample from experiment LS04SR5C

1728 3-12-82 DIF SAM SYNROC D LS04 #8
 INITIAL 2THETA- 10.000 DELTA 2THETA- 0.040 TIME INTERVAL- 4.00SEC
 ISM- 9 IBKG- 3 1 TGKA2- TGDSP-CU ND2- 9 SENS- 0.7 NUM- 1 IPF-5

Figure 11 X-ray crystallographic data for a sample from experiment LS04SR9A

Appendix A

New Synroc Phase of Morgan and Ryerson¹⁸

2θ	D_{obs}	D_{calc}	hkl	I/I_0
10.68	8.441	8.416	(111)	3
12.34	7.290	7.288	(200)	2
17.45	5.140	5.153	(220)	1
20.47	4.381	4.395	(311)	1
21.33	4.205	4.208	(222)	2
24.70	3.633	3.644	(400)	<1
26.90	3.339	3.344	(331)	<1
32.13	2.803	2.805	(333)(511)	100
35.08	2.572	2.577	(440)	<1
37.20	2.430	2.429	(442)(600)	21
40.80	2.21943	2.2228	(553)	4
43.25	2.1011	2.1039	(444)	6
44.60	2.0402	2.0410	(551)(711)	6
48.19	1.8957	1.8976	(553)(731)	1
52.00	1.7648	1.7670	(644)(820)	1
53.61	1.7154	1.7178	(660)(822)	43
54.80	1.6808	1.6831	(555)(751)	<1
55.04	1.6740	1.6791	(622)	<1
57.85	1.5989	1.5999	(753)(911)	<1
58.20	1.5901	1.5904	(842)	<1
60.85	1.5268	1.5280	(931)	<1
63.67	1.4656	1.4649	(755)(771)(933)	33
65.57	1.4275	1.4293	(862)(10,20)	<1
66.86	1.4018	1.4023	(666)10,22)	6
71.04	1.3290	1.3316	(10,42)	2
74.96	1.2687	1.2687	(882)(10,44)	2
77.38	1.2349	1.2363	(973)(11,33)	2

New Synroc Phase of Morgan and Ryerson¹⁸ (Continued)

2 θ	D _{obs}	D _{calc}	hkl	I/I _o
78.92	1.2145	1.2147	(884)12,00)	4
81.55	1.8179	1.8227	(10,64,)(12,22)	<1
87.61	1.1479	1.1470	(993)(11,55)(11,71)(13,11)	9
90.54	1.0856	1.0864	(10,84)(12,60)	7
102.5	0.9918	0.9918	(10,10,4)(12,66)(14,42)	7
111.08	0.9350	0.9350	(999)11,11,1)(13,75)	8
119.67	0.8914	0.8920	(11,11,5)(13,77)	2
122.90	0.8778	0.877	(14,84)(16,42)	2
127.55	0.8590	0.8589	(12,12,0)(16,44)	4
139.35	0.8217	0.8213	(13,11,5)(15,93)(17,51)	12
144.10	0.08099	0.8098	(12,12,6)(14,88)(16,82)(18,00)	9

a = 14.576 Å cubic (face centered), probably pseudo-cubic

Believed (possibly) similar to Murataite

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