FEASIBILITY OF MELTCASTING STRONTIUM FLUORIDE TO PRODUCE HIGH-DENSITY HEAT SOURCES

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ABSTRACT

A modest proof-of-principle effort has been conducted to investigate melt casting as a process for compacting SrF_2 to near theoretical density. A nonradioactive SrF_2 mixture, similar in chemical composition and method of preparation to SrF_2 encapsulated at the Hanford Waste Encapsulation and Storage Facility (WESF) was used for the test evaluations. Hard, dimensionally stable, monolithic ingots that are >98 percent of theoretical density have been produced. Significant chemical purification from Al, Fe, Cr, Ni, Na and Zr has been demonstrated.

INTRODUCTION

Fission product strontium, a byproduct from the processing of irradiated fuel, has been used as the energy source for over 60 radioisotope thermoelectric generators (RTGs) used in terrestrial applications. The only current source of this material is the encapsulated strontium fluoride stored in the Hanford Waste Encapsulation and Storage Facility (WESF) storage basins. Over 30 million curies of strontium-90 have been encapsulated in 427 capsules and placed in storage. The primary mission of B-Plant and WESF has been the conversion of highly concentrated strontium solutions to dry stable solids in the form of strontium fluoride, double encapsulated in metal containers. Manufacturing high-density strontium capsules for use in RTGs or other thermal converters was not a primary consideration. As a result, highest achievable density and chemical purity were not obtained. The highest-wattage capsules currently in the WESF storage basins have strontium fluoride densities of 3.2 to 3.7 g/cm^3 (75 to 85 percent of theoretical density) and thermal outputs of from 660 to 760 watts.

For many heat sources or electrical power generator applications, an optimized system requires encapsulated strontium fluoride of higher power density (W/cm^3) than currently available. The use of strontium fluoride of lower power density increases the size and weight of the generator, increases the heat losses, and decreases the power conversion efficiency. Fission product strontium with a higher $^{90}Sr/Sr$ isotopic ratio cannot be obtained unless waste from future Purex operations is processed in B-Plant and WESF. That leaves improvements in bulk density and chemical purity as the only strontium fluoride parameters affecting power density that can be modified.

Proof-of-principle experiments were conducted in 1983 to investigate melt casting as a possible alternative to hot pressing for densifying SrF_2 for heat or power source use. The primary requirements were that the cast cylindrical ingots be free of surface or interior voids, have near theoretical density, have a predictable uniform diameter, and be strong enough to withstand handling. Chemical purification was not an initial requirement but has proved to be an attractive process feature.

DESCRIPTION OF EXPERIMENTS

Equipment

The melt-casting tests were performed in a cylindrical, water-cooled, stainless steel vacuum chamber 60 cm diameter by 90 cm high. The vacuum chamber was equipped with side and top viewing ports. Melting and casting crucibles were heated by thermally insulated induction coils inside the vacuum chamber. A few tests were performed using tantalum crucibles, but most of the tests were performed in melting and casting crucibles fabricated from graphite. A mechanical roughing pump and a diffusion pump were used to obtain the necessary gas pressure inside the chamber. After closing the chamber and before high-temperature operations, air was removed from the chamber and replaced with argon to protect the graphite or tantalum crucibles from oxidation.

Preparation of Strontium Fluoride

Several 11.5 kg batches of nonradioactive SrF_2 feed material were prepared and used. Weighed amounts of the nitrates of Sr, Fe, Cr, Ba, Ca, Cd, Al, Mg, Mn, Nd, Ni and Pb were dissolved in water. Solid sodium fluoride was added to the solution to precipitate the fluorides. The slurry was digested one hour at 80°C and then filtered through #42 filter paper. The filter cake was dried at 125°C in a drying oven. Weighed amounts of KF, NaF and ZrF_4 were added to the dried precipitate and thoroughly mixed with the precipitate by ballmilling. The blended fluoride mixture was then vacuum dried at 275°C for 24 hours and then fired at 800°C. After firing, the fluoride mixture was again ballmilled.

The normal composition of the fluoride mixture, based on the composition of the feed solution is given in Table I. The composition is similar to that obtained in the WESF SrF_2 operation.

TABLE I

Nominal Composition[a] of the SrF_2 Salt Mixture

Component	Weight
Sr	64.60
F	31.30
Al	0.15
Ba	0.45
Ca	0.15
Cd	0.02
Cr	0.15
Fe	0.22
K	0.12
Mg	0.02
Mn	0.01
Na[b]	1.50
Nd[c]	0.50
Ni	0.15
Pb	0.02
Zr[d]	0.84

(a) Based on composition of feed solution
(b) Can vary depending of washing of precipitate
(c) Nd used as typical of rare earths
(d) Zr will increase in WESF $^{90}SrF_2$ as ^{90}Sr decays

Initial Melting Tests

Pure SrF_2 melts at 1473°C and the vapor pressure reaches one atmosphere at 2489°C. During initial melting experiments performed in graphite crucibles, the impure feed powder was found to melt at a temperature of about 1350 to 1400°C. Three phenomena were observed in the early tests.

They were:

1. Impure feed powder cannot be melted in a high vacuum without excessive splattering as the volatile impurities are released. However, the powder can be melted without significant splattering under an argon pressure of 400 to 250 torr.

2. Iron, chromium and nickel impurities are reduced to metal by reaction with the graphite crucible. When the melts were cooled and removed from the graphite crucible, metal globules containing these elements were found imbedded in the outside surface of the ingots.

3. High density SrF_2 ingots cannot be formed by melting the powder under an argon pressure of 500 to 400 torr and then freezing the molten salt in the melting crucible. Volatile impurities released during the process produce voids in the solidified ingot. When the volatile impurities are vaporized from the molten salt by slowly reducing the pressure inside the vacuum chamber and then restoring the pressure to about 500 torr before the salt is frozen, high density ingots are obtained.

Definitive Melt Casting Tests

The observation that Fe, Cr and Ni are reduced to metal by reaction with the graphite melting crucible prompted the use of separate melting and casting crucibles. A graphite melting crucible was fabricated with a drain hole in the bottom, slightly elevated above the bottom of the crucible. A graphite stopper rod sealed the drain hole during powder loading, melting and outgassing steps. When the stopper rod was raised, the molten salt drained from the melting crucible into a graphite casting crucible positioned directly below the melting crucible. Fine metallic globules of Fe, Cr and Ni remained in the melting crucible attached to the inside surface of the graphite. Some salt also remained attached to the stopper rod and in the trap in the bottom of the crucible. Such salt can be recycled.

When molten SrF_2 is cast into a cold mold, freezing starts at the mold interface and progresses inward. The result is a pipe or cavity that extends from the top part way down the center line of the casting. Piping was minimized by controlled directional cooling of the mold. By adjusting the spacing of the induction coils surrounding the graphite casting mold, it was possible to control the cooling and maintain a bottom-to-top temperature differential during solidification.

The ingot shown in Fig. 1 was cast by this technique. About 0.5 cm was cut off the top of the ingot to remove a small cavity. The maximum and minimum diameters of the ingot were measured at 1-inch intervals down the height of the ingot. The results given in Table II show a range of 0.012 in. between extreme diameter measurements. The density of this ingot was 4.23 g/cm^3 or 99.6% of the theoretical density of pure SrF_2. Several ingots with bulk densities above 4.15 g/cm^3 (98% of theoretical density) have been prepared.

Chemical purification can be achieved by careful control of the crucible temperature and the pressure inside the vacuum chamber. Figure 2 shows the temperature and pressure measurements for the test which yielded the ingot shown in Fig. 1. The pressure inside the chamber was held at about 250 to 150 torr until the charge had melted. The pressure was then reduced to about 0.8 torr over a period of about 65 minutes. Volatile impurities vaporized from the molten salt and condensed on cooler surfaces inside the chamber. When the pressure reached 0.8 torr, the vacuum system was valved off, argon was admitted to the chamber until the pressure reached 500 torr, and then the stopper rod was raised to permit the molten salt to drain from the melting crucible into the casting crucible. Power was reduced which allowed the temperature to fall as shown in Fig. 2. After the furnace had cooled and was opened, residues were recovered from the melting crucible and from the inside of the vacuum chamber. It was obvious that there had been some splattering of material from the melting crucible. The ingot was recovered from the mold. All materials recovered were weighed, sampled, and the samples analyzed. The analyses and the material balance recoveries are summarized in Table III.

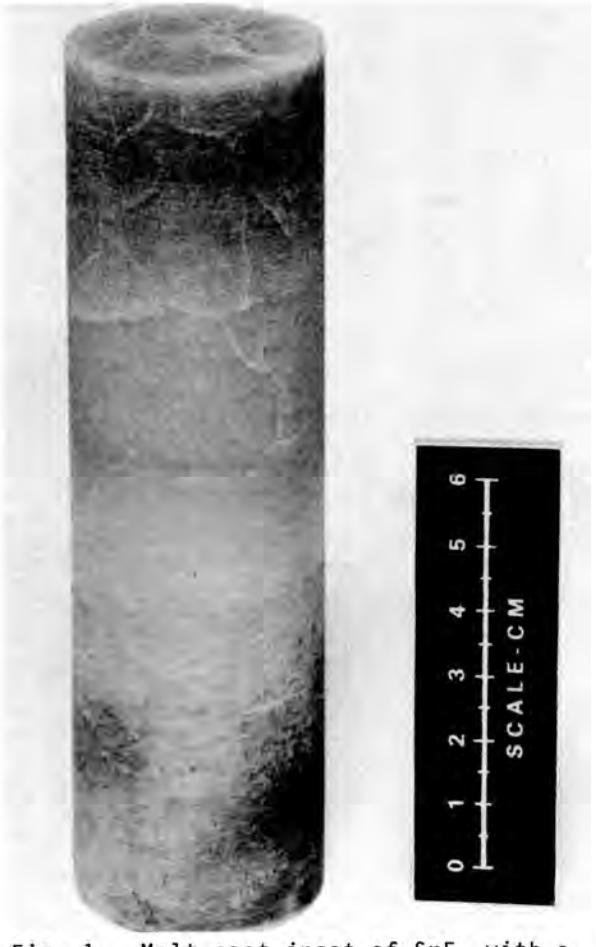

Fig. 1. Melt cast ingot of SrF_2 with a density of 4.23 g/cm^3.

Purity of the SrF_2 was increased to 98.6% but only 80% of the SrF_2 was recovered in the ingot. Twelve percent was recovered from the melting crucible and 7% from the vacuum chamber. The residue recovered from the melting crucible could be recycled. Refinements in equipment design and in the control of both temperature and pressure should significantly reduce strontium holdup in the melting crucible and splattering into the vaccum chamber.

A final test was made to evaluate impurity decontamination using feed material containing much higher concentrations of NaF, SiF_4 and ZrF_4. Due to equipment problems, the vacuum chamber was pumped down to only about 50 torr before the molten salt was drained into the casting mold. As a result, the recovered ingot was not purified. The ingot was remelted and the pressure reduced to 0.4 torr over a period of about 60 minutes before refilling the chamber with argon and casting the molten salt. The recovered ingot had uniform dimensions and a density of 4.23 g/cm^3. The chemical analyses are given in Table IV. The good impurity decontamination achieved is probably more a result of the lower pressure than the recasting.

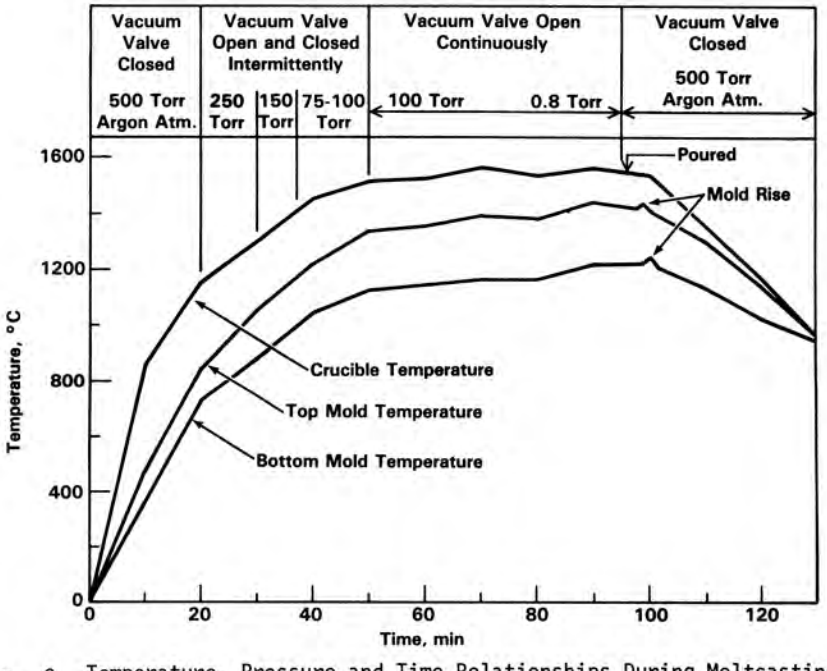

Fig. 2. Temperature, Pressure and Time Relationships During Meltcasting of Ingot in Fig. 1.

TABLE II

Variation in Diameter of Cast Ingot

	Top	1st Inch	2nd Inch	3rd Inch	4th Inch	Bottom
Maximum Diameter (in.)	1.451	1.451	1.454	1.449	1.448	1.446
Minimum Diameter (in.)	1.448	1.446	1.446	1.444	1.446	1.442

Range Between Extremes 1.442 to 1.454 = 0.012 in.

TABLE III

Analysis of Material Balance Recovery From Melt Casting

Compound	Melting Charge wt=900g Analysis[a] (wt%)	Recovered Ingot wt=700g % of charge=78 Analysis (wt%)	% of Compound in Charge	Residue Recovered From Melting Crucible[b] wt=116g % of Charge=13 Analysis (wt%)	% of Compound in Charge	Residue Recovered From Vacuum Chamber wt=75g % of Charge=8 Analysis (wt%)	% of Compound in Charge	Material Balance Accountabili (%)
AlF_3	0.33	ND		0.77	30	3.34	84	117
BaF_2	0.65	0.45	54	2.2	44	0.87	11	107
CaF_2	0.23	0.21	71	0.23	13	0.25	9	85
CrF_3	0.15	0.014	7	0.55	47	0.33	18	120
FeF_3	0.19	0.016	6.6	0.24	16	0.25	11	107
NaF	2.06	0.06	2.3	5.04	32	11.8	48	54
NdF_3	0.38	0.36	71	0.35	12	0.31	7	88
SrF_2	95.2	98.6	80.6	88.1	12	76.5	7	99.7
ZrF_4	0.77	0.24	24.2	1.86	31	1.94	21	84

(a) Analysis by Inductively-Coupled Plasma/Optical Emission Spectroscopy
(b) Does not include 1 gram of metal globules recovered separately

TABLE IV

Chemical Purification Achieved With Lower-Pressure Vaporization of Impurities

Impurity Material	Feed Material (wt%)	First Cast Ingot (wt%)	Recast Ingot (wt%)	Impurity Decontamination Factor
AlF_3	0.28	0.07	0.04	7
BaF_2	0.65	0.68	0.21	3
CaF_2	0.26	0.23	0.31	1
CrF_3	0.26	0.16	0.02	13
FeF_3	0.34	0.03	0.04	9
NaF	5.04	3.2	0.13	39
SiF_4	9.34	1.35	0.02	7100
ZrF_4	9.34	4.63	0.82	11

TABLE V

Comparison of Melt Casting and Hot Pressing for Use in WESF

Areas of Comparison	Melting Casting	Hot Pressing
Probability of successful development for use in WESF	High	High
Product Density	>95% TD	>95% TD
Equipment off-gas control	Requires careful off-gas cleaning	Less off-gas cleaning requirement than melt casting
Chemical purification	Has potential for significant purification	Has potential for slight increase in impurity contamination
Product ingot dimensional control	Adequate	Very good
Effect on WESF throughput	High probability of adequate throughput	Would reduce throughput
Equipment operability in a hot cell	Comparable to current WESF operations	More complicated than melt casting
Equipment maintainability in a hot cell	Comparable to current WESF operations	More complicated than melt casting
Effect on preparation of feed powder	Can probably eliminate current high temperature drying step	Requires dry, uniform powder
Capsule compatibility	Potential for improved capsule compatibility due to reduced impurities	
Capsule power density	Significantly increased power density because of purification	

COMPARISON OF MELT CASTING WITH HOT PRESSING

Table V shows a comparison of melt casting with hot pressing for densifying SrF_2. Hot pressing is superior to melt casting in three areas: it is a developed technology, it has been used in hot cells for many years, and it requires a significantly lower temperature and less off-gas cleaning.

Although melt casting is done at a somewhat higher temperature, operating at atmospheric pressure or less leads to a significantly simpler process. No high-pressure equipment or hydraulic fluids are required; thus, the in-cell operation and maintenance may be simplified. The greatest advantage of melt casting over hot pressing is the potential for purification during the melt-casting process. The preliminary decontamination factors observed appear sufficient to remove most initial impurity. Furthermore, melt casting appears capable of removing from 80 to 95% of the decay-product zirconium present in stored strontium fluoride. Such purification may result in an increased power density of up to 15% in melt casting of SrF_2 from capsules currently in the WESF storage basin. This purification is in contrast to a probable small increase in impurity content that is expected to occur during material handling prior to hot pressing. Melt casting is believed to have a higher throughput rate and can digest a lower quality feed material than hot pressing.

SUMMARY

Sufficient work has been done to provide a high degree of confidence that melt casting could be developed into a reliable process for use in WESF. The work remaining to be done is mostly equipment development. The work done to date has shown that SrF_2 ingots with bulk densities that are greater than 98% of the theoretical density of pure SrF_2 can be cast to closely controlled sizes. The cast ingots have good physical strength and can be readily cut to any desired length with a ceramic saw. With the exceptions of CaF_2 and BaF_2, good chemical purification is obtained from impurities in the WESF product. A decontamination factor of 3 to 10 from the zirconium daughter is a significant advantage in improving the power density of aged material.

ACKNOWLEDGMENT

This work was supported by the U. S. Department of Energy under Contract DE-AC06-76RLO 1830.