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Letter to the Editors

Development of CaF_2 special refractory components

Abhijit Ghosh, D.D. Upadhyaya *, Ram Prasad, A.K. Suri

Materials Processing Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

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Abstract

Among the non-oxide refractories, the fluorides of Ca and Mg are of considerable importance in the processing of reactive metals and alloys in nuclear industry. This work deals with the development of specific CaF_2 shapes for casting of uranium metal ingots. Studies were carried out in optimizing the slip properties to fabricate dense green components which on sintering at 850 °C attain a theoretical density of approximately 85%. An important feature of this work is in providing a synergistic approach in waste recycling and, as well, in maintaining the assured high purity of the metal produced.

1. Introduction

Refractories are widely employed in construction of different types of industrial furnaces, fireboxes and heat treatment equipment. The essential property requirements for such materials include high melting point, ability to withstand the effects of structural loads at operating temperature, minimal change in volume in the operating temperature range and good spalling resistance and chemical inertness during exposure to service conditions [1]. Oxide ceramic materials are largely used as high volume refractories for such applications, however, non-oxide refractories are not uncommon, e.g. graphite crucibles are used extensively for melting various ferrous and non-ferrous metals [2,3].

Among the fluoride materials, magnesium fluoride (MgF_2) and calcium fluoride (CaF_2) are preferred for processing of nuclear materials in magnesio-thermic and calico-thermic reactors, respectively. Generally, reduction of anhydrous uranium tetrafluoride (UF_4) with calcium and magnesium is carried out in stainless steel reactor vessels provided with a ceramic lining, e.g. of alumina. Similarly, for ingot casting, alumina-coated graphite moulds are employed. Quality of the refractory lining in these two steps is critical for maintaining the stringent specifications with respect to species of higher neutron absorption cross-section and certain other metallurgical impurities such as O, N and C, in the final fuel charge.

In the present work, CaF_2 crucibles suitable for handling uranium melts have been developed as a replacement for conventional alumina-lined graphite shapes. These components provide significant benefits, such as (i) waste recycling, (ii) containment of residual radioactivity and (iii) ensuring a high level of purity in the processed metal charge.

2. Experimental

The as-received CaF_2 slag, being coarse, was subjected to ball milling for 50 h duration in an aqueous medium. The dried, finely ground material was then characterized for particle size distribution using a laser granalometer (Horiba LA-500). In order to establish the optimal firing treatment for the products, the green pellet samples (19.0 mm diameter $\times$ 10.0 mm height) were prepared by cold compaction at 240 MPa. Their densification behaviour was studied in the temperature range 850–1150 °C. The liquid displacement method was used for evaluation of bulk density and porosity of the sintered samples.

For fabrication of larger shapes the slip casting technique was employed. The ground CaF_2 powder

* Corresponding author. Tel.: +91-22 559 3925; fax: +91-22 550 5151.

E-mail address: ddupad@apsara.barc.ernet.in (D.D. Upadhyaya).

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suspension (slip) was prepared under different pH conditions using citric acid and polyethelene glycol (PEG) as additives. Suitable slips could be prepared using a solid loading of 72.0–80.0 wt% with 1.0 wt% PEG, at pH 3.8. Excellent control on drying shrinkage and mould release could be obtained under these conditions. Final firing was carried out in an electric (Kanthal) furnace at 800–950 °C range for 2–6 h.

3. Results and discussion

The common industrial practice of uranium metal production involves metallo-thermic reduction of anhydrous uranium tetrafluoride as

$$UF_4 + 2Ca \rightarrow U + 2CaF_2; \quad \Delta H = -134.0 \text{ kcal}, \qquad (1)$$

$$UF_4 + 2Mg \rightarrow U + 2MgF_2; \quad \Delta H = -83.5 \text{ kcal}. \qquad (2)$$

Looking into the cost effectiveness of the process, each of the above elemental reductants has its own merits [4]. The fluoride slag generated in the above reactions is leached for U metal value and disposed as waste product. A certain low level of radioactivity is carried in the waste at the disposal stage. The radiation fluence levels measured for a typical batch were 1.0 mR h^{-1} for β and 0.1 mR h^{-1} for Υ activity. The slag produced is of nuclear purity and in the intermediate stage, it could be processed for use in uranium containment vessels such as reactor lining and fabrication of ingot casting moulds, with various advantages.

Fig. 1 presents the particle size distribution of ball-milled CaF_2 powder. It shows an ideal monomodal distribution with more than 80.0% of the particles below 10.0 μm in size and the median value at 6.3 μm. Slips prepared from such powder were very thick and non-pourable if the pH was kept above 6.0. Under highly acidic conditions (pH < 3.0), the slip properties were also not acceptable, as the material reacted with the plaster of Paris moulds. This was evident from spot formation observed on the mould surfaces. A similar observation on mould corrosion was also made by Haroun and El-Hout [5] for a natural fluorspar system. Masson et al. [6] successfully carried out the slip casting of CaF_2 in ethyl alcohol, but the common practice is to use an aqueous medium with low pH value for better slip properties. Bieler [7] observed that the lowest viscosity of CaF_2 slip in an aqueous medium is obtained at a pH value below 6.0. However, casting of a coarse grain slip with higher viscosity could be achieved at a pH between 7.2 and 7.5, to keep the coarse grained powder in suspension. A basic slip using commercial deflocculant (Darvan No. 7), was also reported by Cowan [8].

In our experiments, a stable and flowable slip could be prepared by using 1.0 wt% PEG and maintaining the pH at 3.8. Cylindrical samples cast from the slip with 72.0% solid loading achieved a green density of 55.0% theoretical density (TD), which is about 5% higher than that for the cold pressed compacts (at 240 MPa). Densification behaviour of both types of compacts was investigated in the temperature range 850–1150 °C. The soaking period was varied between 2 and 6 h. Results are presented in Fig. 2, for a typical 2 h sintering schedule. In this temperature regime a reasonably linear consolidation behaviour is depicted for the CaF_2 particulate system. At each temperature, the sintered density of slip cast samples is higher than for the cold-pressed case. This is evidently the reflection of a higher green density achieved in the slip casting method.

When the solid loading was increased to 80.0 wt%, the result was a green density of ~60.0% TD. Cast samples of this slip on sintering, for example at 850 °C for 2 h attained a density of 85.0% TD. This slip was thus used for fabrication of cylindrical crucibles of size OD = 100 mm, ID = 85.0 mm and height 120.0 mm. On sintering, the inner drained-surface of the crucibles developed a smooth surface texture not requiring any post-firing finishing operations. Evaluation of components

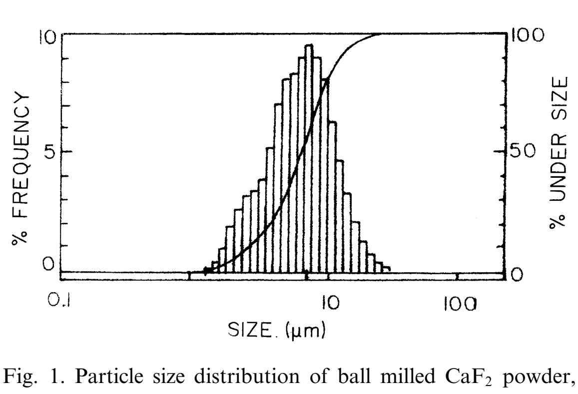

Fig. 1. Particle size distribution of ball milled CaF_2 powder, showing a median particle size of 6.3 μm.

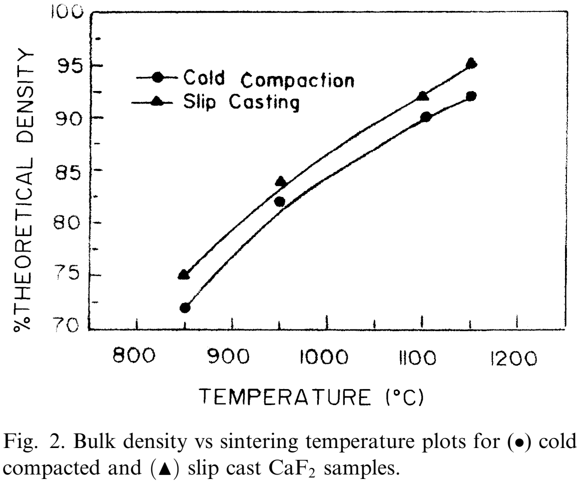

Fig. 2. Bulk density vs sintering temperature plots for (•) cold compacted and (▲) slip cast CaF_2 samples.

for intended application was simulated by thermal cycling from 1050 °C to room temperature. These air-quenched samples did not develop any visible cracks on surfaces even after five cycles. However, in actual plant practice the casting moulds are used in a preheated (~600 °C) condition to minimize the thermal shock damage. The process flow sheet was repeated for MgF_2 slag. Only difference in behaviour was with respect to the sintering temperature being about 100 °C lower, to achieve an equivalent level of densification.

4. Conclusions

1. It has been established that the stable and flowable slip can be prepared with solid loading of up to 80.0 wt% by suitably adjusting the slip preparation parameters. Special refractory shapes having bulk density of ~85% TD were fabricated by sintering at 850 °C.
2. A special significance of the work is in terms of containment of radioactive waste by recycling the slag in the form of special refractory components. The nuclear purity slag is recovered as a valuable resource and has an important role in preventing the impurity pickup associated with the interaction of uranium melt with the refractories.

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