

Influence of Different Sintering Temperatures on Simulant Material for Experiment of Melt Coolability

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Received 4 April 2017; Revised 24 July 2017; Accepted 27 July 2017

Abstract

Simulant material is similar to the corium of the nuclear reactor, which is used for the study of melt-coolability on laboratory scale. The analysis of melt coolability helps us to mitigate the severe accident in the nuclear reactor. Calcium borate simulant material has been synthesized by thermal treatment method via mixing of 30 % CaO + 70 % B₂O₃. The effect of different sintering temperatures on the density, thermal stability, micro structural study and crystalline structure of the prepared simulant material was studied. The sintering time was kept constant for all heat treated simulant materials. The resultant compound was characterized by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Fourier Transform Infrared spectroscopy (FTIR) and Thermal Gravimetric Analysis (TGA). The XRD patterns of simulant material at heat treated temperature 750 °C, 850 °C, 950 °C, for one hour, revealed that the crystalline peaks of calcium oxide, calcium mataborate and mostly single phase of heptaxotetrateborate respectively. The FTIR spectrum of simulant material sintered at temperature 750 °C, 850 °C and 950 °C for one hour revealed that the functional group of triangular BO₃⁻, OH, tetrahedral BO₄⁻ etc. Around 6 – 7% mass loss was observed when the material was heated up to about 450 °C under the TG analysis, beyond that, the mass was decreasing almost linearly and it was about 7.5% at 900 °C due to moisture and other molecules and gases. The moisture content was found to be 5.3 – 4.2%, by weight loss of sample when heated in rapid dryer for a period of two hour.

KEYWORDS: Sintering temperature; Meltcoolability; Calciumborate; Calcium heptaxoborate

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Introduction

Post Fukushima severe accident research has become a necessity to ensure safety of nuclear power plants against the low probable yet high consequence severe nuclear accidents. During such scenarios the core melt down becomes a concern being highly radioactive, chemically reactive at a very high temperature of around 3000 K. To mitigation such scenarios (or event) understanding of the core melt behavior is of time importance. It is practically not possible to conduct experiments with actual core melt due to radioactive environment and being highly expensive so simulant materials having similar thermo physical properties as that of core melt are used for different kind of studies. Many simulant materials have been used in different

experiment with different laboratory which has similar properties as well as the corium properties except harmful radiation. The name of simulant materials like as Cerrobend, NaNO₃-KNO₃ salt, CaO-B₂O₃ binary oxide mixture has been used in RIT experiment [1]. The KAPOOL and KAJET experiments have been used thermite for the study of melt coolability experiment [2]. Different binary simulant CaO-B₂O₃, WO₃-CaO, WO₃-Bi₂O₃, MnO-TiO₂, Bi₂O₃-TiO₂ and Bi₂O₃-CaO have been performed at KTH in the DEFOR tests [3]. In these simulant materials some are more toxic and some less toxic for health and nature. In between CaO-B₂O₃ is nontoxic as well as user friendly. Which has been used such an established simulant material [4]. The study of quenching of simulant material with different methods has been done [5]. The addition of B₂O₃

with-in CaO increases activation energy. This indicates that B₂O₃ acts as a network former but it reduces viscosity simultaneously. The reason why the addition of B₂O₃ reduces viscosity in spite of increasing activation energy is thought that it decreases frequency factor effectively. The frequency factor is mainly dependent on the activation energy but it seems to have a relation with melting temperature. The comparisons of thermo physical properties are presented in table no.1. The addition of B₂O₃ also reduces melting point of CaO [6] remarkably, consequently the super heating is so high that gives more holes available in liquid state structure resulting in lower viscosity.

Table 1 Comparison of thermo physical properties of corium with CaO-B₂O₃

Property	CaO-B ₂ O ₃	Corium
Melting point	1050 °C	2650 °C
Density (Kg/m ³)	2500	7450
Thermal Conductivity (L) (W/mk)	3.0	3.0
Thermal Conductivity (S) (W/mk)	2.0	2.5
Specific heat (L) (J/kg K)	2200	540
Specific heat (S) (J/kg K)	129	410
Viscosity (Pa-s)	0.14	0.12

Materials and Methods

Preparation of samples

The analytical grade (AR) high purity B₂O₃ (average particle size 50µm) and CaO (average particle size 10µm) powders were used directly without further purification. The fix composition of powder 30 % CaO and 70 % B₂O₃ (by wt.) was taken and mixed to achieve near homogeneous level using motor pressure at room temperature. The mix powder was charged in a ceramic crucible and placed in electric muffle furnace, allowing the evolution of the gases formed in the course of the reaction; it is then sintered for 1hr at 750 °C, 850 °C, and 950 °C.

Characterization techniques

X-ray diffraction patterns of the samples were recorded with Cu Kα ($\lambda = 1.54060 \text{ \AA}$), using a Panalytical X Pert Pro diffractometer. Diffraction intensity was measured in the 2θ range of 20° – 70°, at 40 kV, 40 mA and at the scan rate of two degree per minute. Microstructural study was carried out under field emission scanning electron microscope [Nova Nano FE-SEM (FEI)]. FT-IR [using spectrum 2 PERKIN ELMER] spectrum of the sample was recorded using KBr pellet technique in the range of 4000 – 400 cm⁻¹. The density of the heat treated simulant material was measured using ME-DNY-4 density kit. The

measurement of TGA was carried out using STA 6000 PERKIN ELMER at the heating rate of 10 °C min⁻¹. with N₂ as the purging gas. The moisture content was determined by weight loss of sample using rapid dryer for a period of two hour. All tests were done at room temperature.

Results and Discussion

XRD pattern

The XRD patterns showed (Fig. 1, plot a) the crystalline structure for calcium oxide and calcium borate compound and sintered at 750 °C. Furthermore, with increasing the sintering temperature from 750 °C to 950 °C, the dominate phase of CaB₂O₄ is still remaining and at higher temperatures, other phases of CaB₂O₄ (space group Pna 21(33)) and CaO peaks disappeared and some new peaks belong to meta-borate (CaB₂O₄) and heptaxotetra borate (CaB₄O₇) become visible. The XRD peaks presented at 2θ values of 27.97°, 29.41°, 30.63°, 32.27°, 36.05°, 37.43°, 42.57°, 44.35°, 45.77°, 48.01°, 53.97°, 64.25° and 67.43° matching with the (020), (210), (040), (111), (313), (200), (240), (051), (224), (006), (220), (311) and (222) crystalline planes of the cubic structure and orthorhombic structure of calcium oxide and calcium meta-borate at 750°C (ICDD PDF 82-1690, 32-0155), as shown in Fig. 1, plot (b), the observed peaks at 2θ values of 24.71°, 26.5°, 28.21°, 29.93°, 32.75°, 34.77°, 36.21°, 37.75°, 40.51°, 42.71°, 47.29°, 48.33°, 49.57° and 54.25° matching with the different planes (301), (112), (200), (210), (220), (131), (-420), (501), (141), (240), (122), (-423), (311) and (222) crystalline planes of the orthorhombic and monoclinic structure of calcium meta-borate and some calcium heptaxotetra-borate at 850°C and as shown in Fig. 1, plot (c), the peaks observed at 2θ values of 24.25°, 25.89°, 27.27°, 29.07°, 29.69°, 32.67°, 36.25°, 37.91°, 38.51°, 39.97°, 44.87°, 46.97° and 47.91° matching with the (012), (112), (202), (031), (-122), (222), (-402), (041), (141), (430), (142), (611) and (531) crystalline planes are belong to calcium heptaxo-tetra-borate (ICDD PDF 83-2025) at sintering temperature of 950 °C. The peaks are denoted by 1, 2, 2* and 3 as shown in Fig. 1. The notation 2 and 2* are different in only space group of calcium-borate, the space group for notation 2 and 2* are Pnca (60) and Pna 21 (33) respectively.

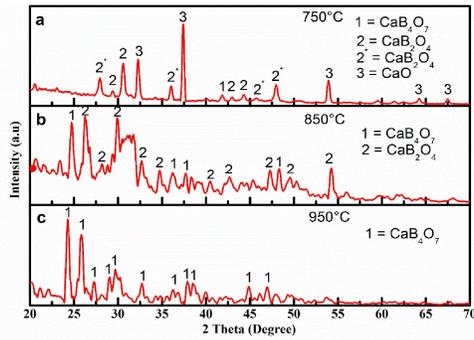


Fig. 1 X-ray diffraction patterns of sintered at (a) 750 °C, (b) 850 °C, (c) 950 °C.

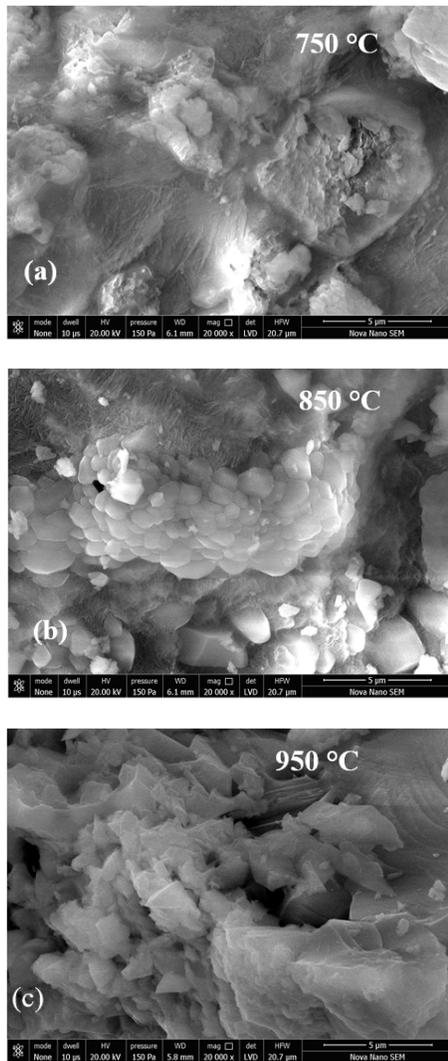


Fig. 2 SEM image of simulant material 30 % CaO + 70% B₂O₃ sintered at (a) 750 °C, (b) 850 °C, (c) 950 °C.

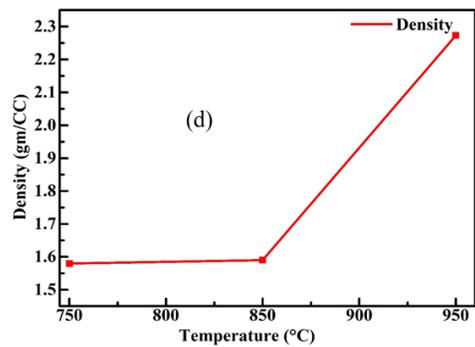
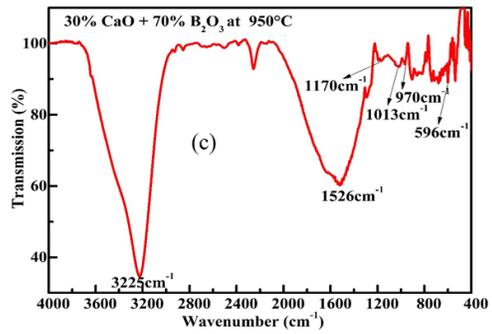
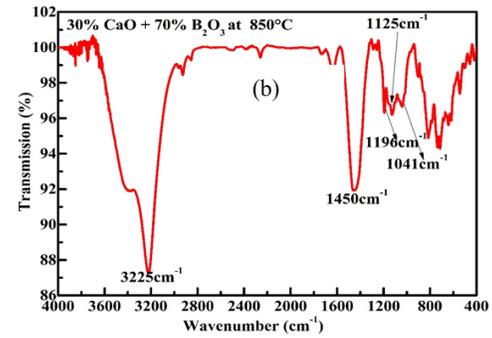
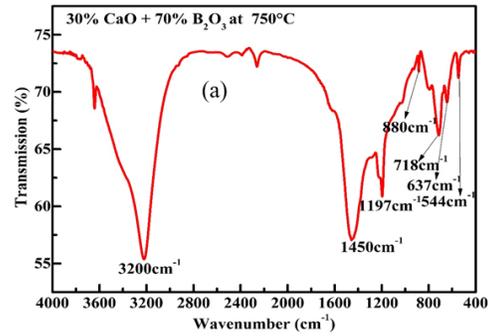


Fig. 3 FTIR spectra for 30 % CaO + 70 % B₂O₃ simulant material sintered at (a) 750 °C, (b) 850 °C, (c) 950 °C, (d) Density of 30 % CaO + 70 % B₂O₃ simulant material sintered at temperature 750 °C, 850 °C, 950 °C.

Micro structural analysis

SEM micrographs of the as sintered simulant material at temperature 750 °C, 850 °C and 950 °C are shown in Fig. 2. In figure (a), different phases with different morphologies are seemed to be present in which might of calcium oxide and calcium borate. As temperature rose to 850 °C, the morphology of the particles was changed (Fig. 2b) which should be due to the formation of calcium borate and calcium tetra-borate as confirmed by XRD. In Fig. 2 (c) almost a single type of particle shape is observed which may be due to the increased percentage of calcium tetra-borate at 950 °C, as also confirmed by XRD analysis.

FTIR analysis

FTIR spectra of sintered sample at different temperatures are shown in Fig. 3 (a, b, c). As can be seen, the band at 3,200 cm^{-1} , 3,225 cm^{-1} is assigned to the OH bending mode. This is relating to moisture in simulant material sample. The absorption peaks at 637, 880 and 1,450 attribute to borate network according to figure 3(a). The vibration modes of the borate network are mainly active in three IR spectra region : 850 – 1,100 cm^{-1} associated with the B-O stretching of tetrahedral BO_4^- units, and 600 – 800 cm^{-1} associated with bending vibrations of various borate segments and a band at around 700 cm^{-1} , which corresponds to bond bending of B-O-B bridges in the boron-oxygen network [11–14]. The band is sifted to left side due phase conversion in tetra-borate from band 1450 to 1,526 cm^{-1} in Fig. 3 (c). The change in oxidation state is most important factor in predicting the absorption frequency for an inorganic group, more important than small changes in the bond order [15]. As a general rule, as the charge increases on the central atom, the atom becomes more electronegative, and the force constant consequently increases. Therefore, the frequency of absorption also increases. The density of the simulant material increased with increase of sintering temperature as shown in Fig. 3(d), due to decomposition of phase from CaB_2O_4 to CaB_4O_7 as confirmed from phase analysis of XRD pattern.

TGA analysis

TG curve of the sintered samples at different temperature are shown in figure 4, with a heating rate of 10 °C min^{-1} . It measures the rate and amount of change in the weight of a material as a function of temperature in the inert atmosphere. The measurements were carried out from ambient temperature to 900 °C. TG curve of all three

sintered sample showed weight loss around 7 wt% at 450 °C. While almost no further weight loss appeared with increasing temperatures. This weight loss is most probably due to trapped moisture in the simulant material and decomposition of phase which is in agreement with FTIR results (figure 3 a, b). In the figure 4(b, c), weight loss up-to 200 °C around 4.5 wt% was confirmed using rapid dryer instrument. Remaining weight loss may be due to other volatile molecule and gases in the sample achieved from the atmosphere.

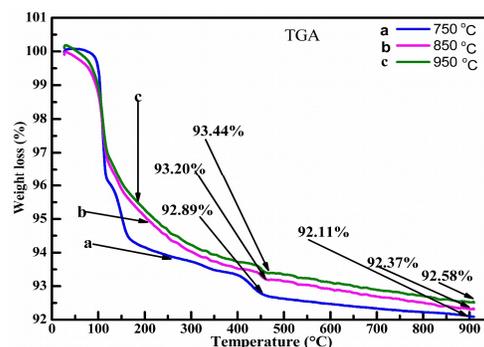


Fig. 4 Weight loss of 30 % CaO + 70 % B₂O₃ simulant material sintered at (a) 750 °C, (b) 850 °C, (c) 950 °C.

Conclusion

The influence of different sintering temperatures on 30% CaO + 70% B₂O₃ simulant material has been studied. At 750 the microstructure mainly comprises calcium oxide and calcium borate. With increasing temperature the calcium tetra borate was formed and finally at 950 °C, the microstructure -mostly comprises of calcium tetra borate as confirmed by XRD and SEM analysis. The density of the simulant material was increasing with increasing percentage of calcium tetra borate. It was observed from TG analysis, about 7 wt% weight of simulant material decreases on increasing in all the three sintering temperature when the materials was heated up-to 900.

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