Influence of temperature on thermo physical properties of non-prototype material (CaO-Fe$_2$O$_3$, 21:79 by wt. %) for nuclear reactor

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In severe accident management, the integrity of the containment structure is a key point to focus the study related to severe accident scenarios that need knowledge of thermo-physical properties of material composition. In the present nuclear accident scenario, nuclear severe accident management is one of the challenging tasks to mitigate the phenomena occurring inside the reactor pressure vessel (RPV). Numerous studies have been done in the past to predict the severe accident phenomena and tried to explore the incidence by using different prototype and non-prototype (simulant) materials. In this context, an initial effort has been made to study the actual phenomena during an accident scenario with non-prototype material CaO-Fe$_2$O$_3$. Initially, the present work involved the study of the material CaO-Fe$_2$O$_3$ powder for thermo-physical property analysis and later, the study will be carried out via melt cool ability of this material in a hypothetical nuclear reactor for analysis and mitigation of nuclear severe accident phenomena. The non-eutectic binary powder mixture of CaO and Fe$_2$O$_3$ has prepared manually by mixing in a mortar for 40 minutes in the ratio of 21:79 by wt. % (21C79F; C refers to CaO and F refers to Fe$_2$O$_3$) which has been confirmed by the phase diagram. Further, pallets were prepared of the non-eutectic binary mixture and heat-treated at 1000°C, 1100°C, and 1200°C for 3 hours in a programmable furnace. The powder form of heat-treated pellets was characterized to analyze thermo-physical properties and to validate as a simulant material (non-prototype) used for the predictive study of a nuclear severe accident. The thermal properties, phase analysis, and morphological studies of the CaO-Fe$_2$O$_3$ (21:79 by wt. %) have been reported in the current research work and analyzed accordingly.

Keywords: CaO-Fe$_2$O$_3$, Thermo-physical properties, Simulant material, Melt cool ability

1 Introduction

The severe accident in the nuclear reactor is initiated due to the melting of core fuel rods in a reactor pressure vessel (RPV) that results from excessive temperature gradient setup and the absence of adequate cooling. The hot molten core can impact the wall of the reactor in-vessel which is the first boundary of safety preventing the leak of radioactive materials in ex-vessel. Hence the coolability of the ex-vessel becomes a necessary part of safety measures to maintain the integrity of the containment structure from the release of radioactive material into the atmosphere as it is the final barrier of safety. The study of a nuclear severe accident has become the matter of interest in which all the previous investigations have been exercised on simulant materials, however, very few studies have been done with prototypes. The purpose of utilizing simulant material for the study of nuclear severe accident management is due to eco-friendly, cheap, availability in comparison of prototype material (uranium oxide and zirconium oxide) and has similar

properties with corium (a liquid form of UO$_2$ and steel) which can be easily handled since it has no any harmful effect on the environment as well as for human beings. The various types of simulant materials that can be used to study the actual phenomena during a severe accident are CaO-B$_2$O$_3$, NaNO$_3$-KNO$_3$, WO$_3$-Bi$_2$O$_3$, MnO-TiO$_2$, Bi$_2$O$_3$-TiO$_2$, and Bi$_2$O$_3$-CaO. Some of these simulant materials have already used by various researchers in the past as explained further. The study of heat transfer along the radial and axial direction from the molten pool and water ingression through the debris was reported using model code (MELCOOL) which was validated through an experiment named core melt cool ability (COMECO) by using 14L of molten CaO-B$_2$O$_3$ (simulant materials)[1]. Agglomeration and debris particle size distribution have been addressed through an experiment (DEFOR-A test) in which hot binary oxidic melt of WO$_3$-Bi$_2$O$_3$ simulant material was poured into a water pool for analysis of debris formation[2].

Since CaO-Fe$_2$O$_3$ is new material and could be considered as a simulant materials for the study of melt cool ability behavior to investigate the severe

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accident phenomena. To utilize $CaO-Fe_2O_3$ as a simulant material in molten form, this should be necessary to mitigate the behavior of thermo physical properties of $CaO-Fe_2O_3$ powder with existing simulant materials and corium. Since very little information are available about $CaO-Fe_2O_3$ powder. Hence it is required to first analyze its thermo-physical properties so that it could mitigate and validate the property of simulant materials. In the context of the microstructural study of current material, some works of literature have been quoted to study the background of $CaO-Fe_2O_3$ in which the various researchers have been contributed to the information about morphology, phase analysis, and thermal stability. The basic thermophysical properties of a eutectic binary mixture of $CaO-Fe_2O_3$ (22:78 by wt. %) have reported that the material is thermally stable near the eutectic range[3]. The physical properties of binary ferrite melt were measured together with ferrite samples and structures that were discussed with the help of physical properties with crystallinity structure[4-5]. Characterization of $CaFe_2O_4$ synthesized by polymer precursor method and reported that the crystallite size increased about 30% when the material was calcined from 500°C to 1100°C which indicates the change in growth mechanisms[6]. Another researcher laid down the thermal expansion, molar volume, and density of melts in the $FeO-Fe_2O_3-CaO$ ternary system[7]. Further, the reaction between CaO and Fe_2O_3 was investigated under the effect of $CO-CO_2$ at a temperature range of 800°C to 1100°C and the effort was made to reveal the information using XRD[8]. The information about the formation of calcium ferrite and its intermediate phases ($CaFe_2O_4$, $CaFe_3O_5$, and $Ca_2Fe_2O_5$) revealed which were confirmed by TGA and XRD using different oxides under a controlled atmosphere[9]. Investigation of calcium ferrite formation using CaO source and measured the value of relative density by linear shrinkage rate test and Archimedes principle. DSC analysis was used to investigate the compositional behavior and calcium ferrite formation at a different heating rate ($\leq 1200°C$)[10]. The activation energy of dicalcium ferrite was found lower than calcium ferrite during the isothermal reduction of $CaO-Fe_2O_3$ and $2CaO-Fe_2O_3$ powder under the effect of H_2[11]. The crystallization behavior of $CaO-Fe_2O_3$ at different composition, cooling rates have been discussed and found good agreement[12-13]. Two phases ($2CaO-Fe_2O_3$, $CaO-Fe_2O_3$) of $CaO-Fe_2O_3$ were found using DSC and XRD investigations and also reported the apparent

activation energy of the phases is -464.16 and -162.16 kJ/mole[14]. The analysis of thermophysical properties of $CaO-Fe_2O_3$ at different soaking times has been conducted and found similar to that of corium[15-16]. Recently, an effect of air quenching of simulant material ($CaO-Fe_2O_3$ and $CaO-B_2O_3$) on its properties has been reported that the morphology, phases, and thermal properties altered when heat-treated at different temperatures[17-18]. The present work is associated with the study of thermo-physical properties of non-prototype material $CaO-Fe_2O_3$ (21:79 by wt. %) for a nuclear reactor as this material is non-toxic, eco-friendly, ease of availability, and economical.

Previous researchers have assessed the data found during the melt coolability experiment by using different simulant materials and discussed the concept of porosity of the target material with different quenching techniques (Top flooding, Bottom flooding, and Indirect cooling) in a hypothetical nuclear reactor. The aforesaid experiment aimed to evaluate the high porosity, agglomeration, and water ingression, coolability of the material which could be led to more heat transfer and cool down the reactor to mitigate the severe accident phenomena. The scope of the best simulant materials is still remaining for more comprehensive research to analyze the physical and thermal hydrodynamic phenomena that appeared during severe accidents. In continuation of this study, a new simulant material $CaO-Fe_2O_3$ (21C79F) has been selected for the study of nuclear severe accident scenarios by quenching behavior of melt coolability technique in the hypothetical reactor. In the present work, an attempt has been taken to analyze the thermo-physical properties of the material before melt coolability.

2 Materials and Methodology

Two oxides, CaO and Fe_2O_3 mixed in the ratio of 21:79 by wt. % (21C79F) in a mortar for up to 40 minutes and a non-eutectic binary mixture $CaO-Fe_2O_3$ was prepared. The ratio of the mixture has been confirmed by the phase diagram as shown in Fig. 1[19]. In the phase diagram, three zones like hypo eutectic, eutectic, hyper eutectic are shown in which the present material belongs to hyper eutectic (non-eutectic material). Three different pellets were prepared of a constant mass of 2 grams in the cylindrical form of diameter 12.17, 12.2, and 12.16 mm with a maximum thickness of 7.78, 7.61, and 8 mm, respectively. The $CaO-Fe_2O_3$ powder was

pelletized under a load of 3.5 tons for a compaction time of 5 minutes. An electric programmable furnace was used for heating pellets. After putting pellets into the furnace, it was heated up to 1000°C (first pellet), 1100°C (second pellet), and 1200°C (third pellet) for constant soaking time. These pellets were heated and hold for three hours soaking time in a furnace at 1000°C, 1100°C, and 1200°C. After heat treatment, the pellets were ground manually and converted into powder form for further characterization. The details of workflow mechanisms of current work are shown in Fig. 2. All the dimensions of pellets were measured before and after heat treatment for weight loss analysis. The weight loss has been determined by the dimensional method.

Further, the characterizations of CaO-Fe$_2$O$_3$ (21C79F) powder have been carried out for with and without heat-treated through DSC (Differential Scanning Calorimetry), XRD (X-ray Diffraction), and FE-SEM (Field Emission Scanning Electron Microscopy) and analysis of thermal properties,

phases, and morphology are reported accordingly. The objective of this research paper is to determine the effect of varying temperatures on the thermo-physical properties of the powder mixture.

3 Results and Discussion

As the sample in the form of pellets were heat-treated at 1000°C, 1100°C, and 1200°C for constant soaking time three hours, the variation in weight was found significantly change due to change in density before and after heating measured dimensionally since it is a physical property of material which is the function of temperature. At 1000°C the weight loss was found as 9% because at this temperature the initial volatile materials were evaporated significantly. But when the sample was put for heat treatment at 1100°C, found maximum weight loss as shown in Fig. 3. This was appeared due to diffusion of molecules resulting in lowering of density as confirmed by SEM. Further, when the sample was heated at 1200°C, the weight loss
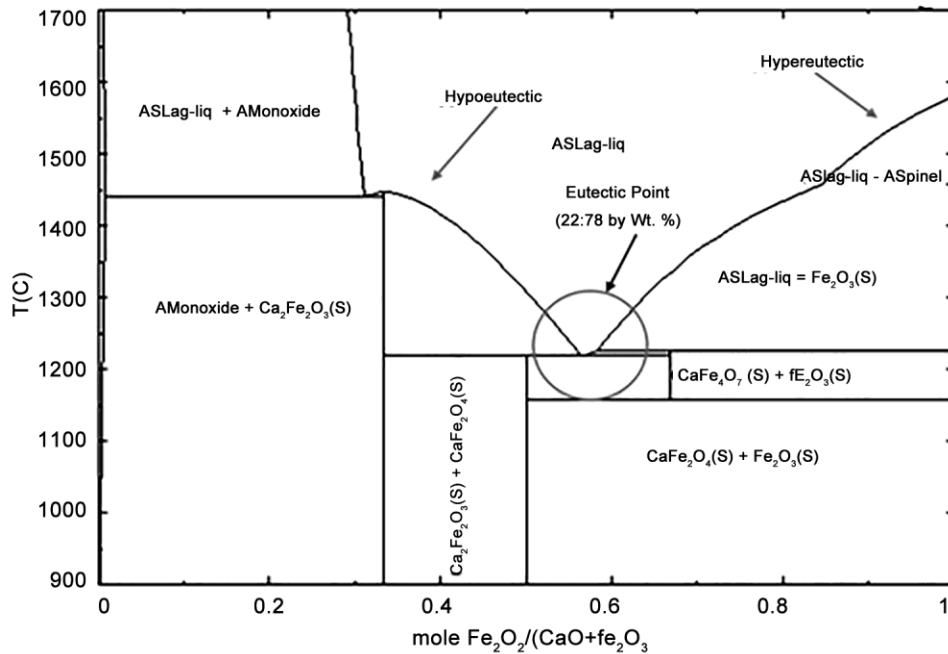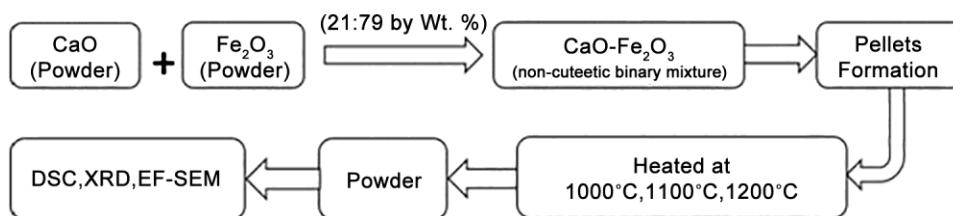

Fig. 1 — Phase diagram of CaO-Fe$_2$O$_3$[19].

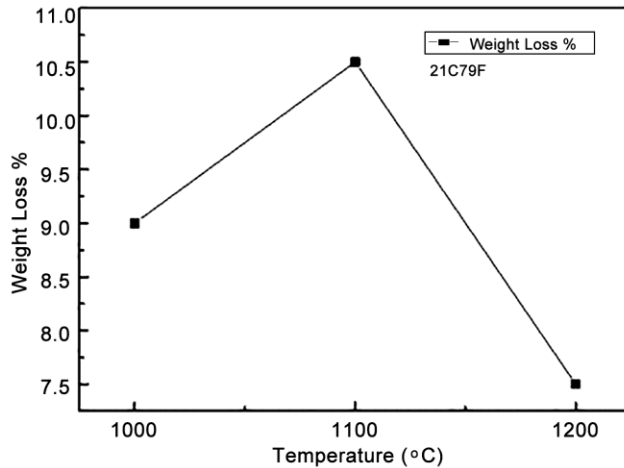Fig. 2 — Work flow mechanism.

Fig. 3 — Effect of heating temperature on weight loss.

decreased due to material agglomeration and saturated diffusion.

3.1 Thermal interaction of CaO-Fe₂O₃for three hours soaking time at 1000, 1100, and 1200°C

Thermal study of CaO-Fe₂O₃ (21C79F) powder was carried out through DSC (NETZSCH DSC 404F3) at a heating rate of 10 K/min and the image is shown in Fig. 4 which reported that the first endothermic peak has developed at 422°C resulting that the removal of moisture and volatile materials in the powder mixture. Another endothermic peak reported the melting point and enthalpy of CaO-Fe₂O₃ was found as 1212°C and 88.16 J/g respectively. The inset image exhibits the melting of powder started at 1192°C and complete transformation into liquid occurred at 1212°C. Figure 5 shows the DSC image of heat-treated CaO-Fe₂O₃ powder at various temperatures and the holding time was kept constant for every heating temperature. When the sample (21C79F) was heated at 1000°C (Fig. 5 a), It needed 159 J of energy (heat of fusion) to melt per unit gram of material and found maximum heat energy i.e. 209 J/g required for complete melting at 1100°C (Fig. 5 b). But heat energy reduced slightly when the sample was heated at 1200°C (Fig. 5 c). The reduction of heat energy is possible due to the heating temperature quite near its melting point and longer duration of soaking time. More specific heat required for material heated at 1100°C in comparison to the remaining two samples heated at 1000°C and 1200°C due to the formation of some unstable phases meanwhile heating. The activation energy of the heat-treated sample is determined by the Arrhenius equation[20] and found that its value increases with increasing heating temperature.
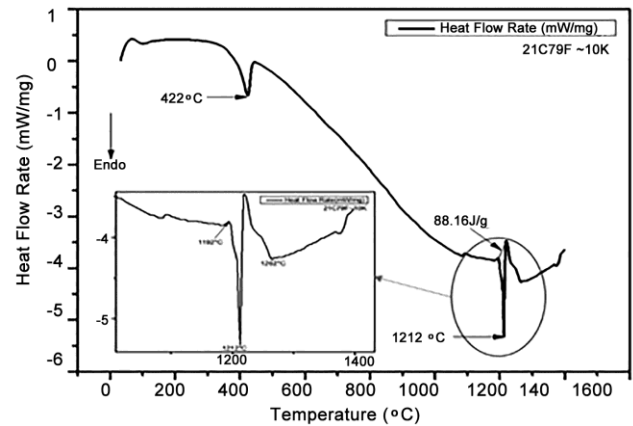

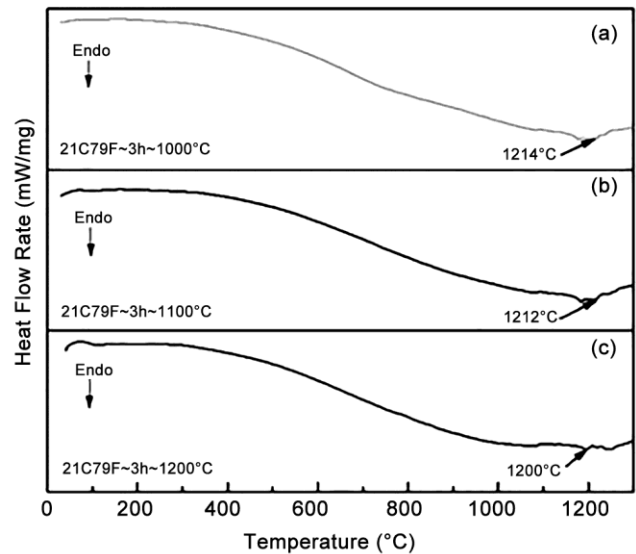Fig. 4 — DSC curve of CaO-Fe₂O₃ (21:79 by wt. %) mixed powder.

Fig. 5 — DSC curve of CaO-Fe₂O₃ heat treated powder at different temperature for constant soaking time.

3.2 Effect of heating temperature on melting point (MP), the heat of fusion (HOF), specific heat (SH), and activation energy (AE)

As the sample (21C79F) is heated at different temperatures, its melting point decreases as the heating temperature (HT) increases because very little energy is required for heating at 1200°C as compared to the remaining two heating temperatures. Further, it has been confirmed from Fig. 6 (a), (b), and (c) the value of heat of fusion (HOF) and specific heat (SH) both initially increased and later on theses value decreased at 1200°C due to heating at near to the melting point and longer time duration. The activation energy required for every temperature (d) increases along with the heating temperature of the material.
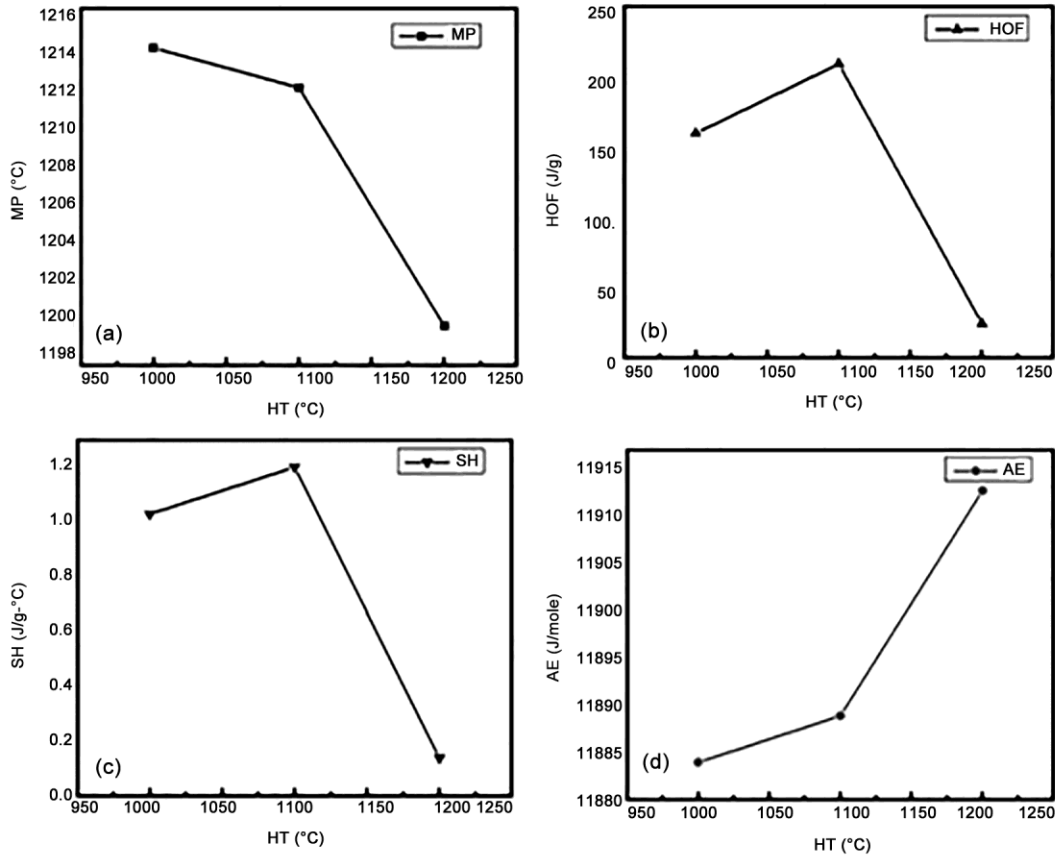
Fig. 6 — Effect of soaking time on (a) melting point (MP), (b) heat of fusion (HOF), (c) specific heat (SH), and (d) activation energy (AE).

3.3 Effect of temperature on the melting point of CaO-Fe$_2$O$_3$

The variation in the melting point of heat-treated CaO-Fe$_2$O$_3$ powder has been shown in Fig. 7. Since the fixed ratio (21:79 by wt. %) of material is heated at 1000°C, 1100°C, and 1200°C for three hours soaking time, no significant variation occurred in the melting point due to heating at various temperature. However melting point reported as quietly decreasing as heating temperature increased, due to recrystallization of material during heating in range of time duration three hours which led to more diffusion rate at high temperature.

4 Micro structural analysis of CaO-Fe$_2$O$_3$ (21C79F) powder before and after heat treatment

For the studies of phase analysis, weight loss and surface morphology of 21C79F, powder of heat-treated pellets was characterized through X-ray diffraction, Thermo gravimetric analysis, and Scanning Electron Microscopy and the corresponding results have been discussed in the context of the heating effect.
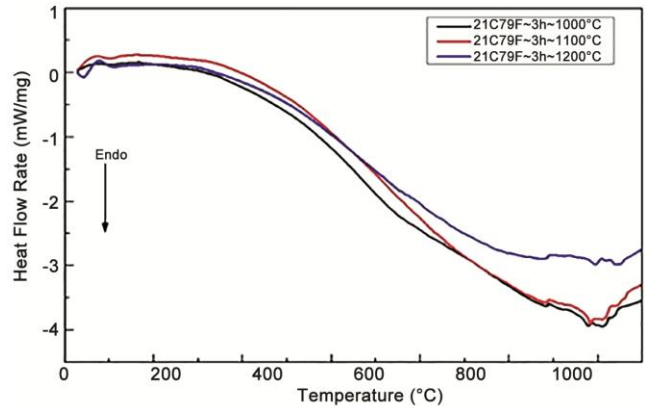

Fig. 7 — Melting point variation of CaO-Fe$_2$O$_3$ pallets heat treated at different temperature.

4.1 Phase analysis of CaO-Fe$_2$O$_3$ powder

The X-ray diffraction (CuKα radiation) of sample (21C79F) powder was carried out before heat treatment and the image is shown in Fig. 8, reported that only two phases appeared of CaO and Fe$_2$O$_3$. Generally ceramics materials are amorphous. Further material was heated in the form of pellets at various

temperatures for three hours and phase analysis have been done in powdery form as shown in Fig. 9 (a), (b), and (c). When the sampleswere heat-treated at 1000°C, 1100°C, and 1200°C for three hours, get recrystallized and various phases were formed during heating. The major phases appeared as $CaFe_2O_4$ (orthorhombic), $CaFe_4O_7$ (monoclinic) which were stable, and at 1200°C the intermediate phases were disappeared. Since all stable phases produced having
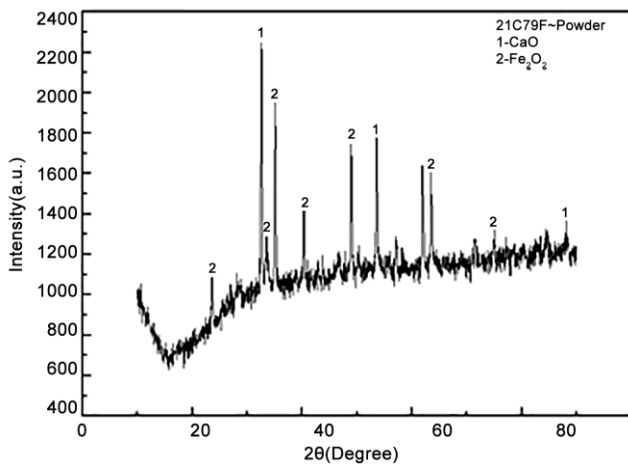

Fig. 8 — XRD pattern of CaO-Fe₂O₃ powder before heat treatment.

a lower melting point if the composition is high CaO content[12].

4.2 Effect of heating temperature (HT) on crystallite size, lattice strain, and dislocation density

The crystallite size, lattice strain have been calculated by the Hall Williamson method[21] of the sample heat-treated at 1000°C, 1100°C, and 1200°C. Dislocation density was calculated with the help of crystallite size and analysis of the effect of heating temperature reported by graphical representation as shown in Fig. 10 (a), (b), and (c). The value of crystallite size increased with increasing temperature up to 1100°C but decreased at 1200°C because the sample was heated near to the melting point for three hours of soaking time. At this temperature, materials are completely recrystallized. Figure 10 (b) reported the variation of lattice strain concerning the heating temperature. According to this, the lattice strain decreased at 1100°C and increased at 1200°C with temperature due to the disappearance of unstable phases. Further, the value of dislocation density remains unchanged till 1100°C but increased significantly at 1200°C which indicates the thermal stability of the material.
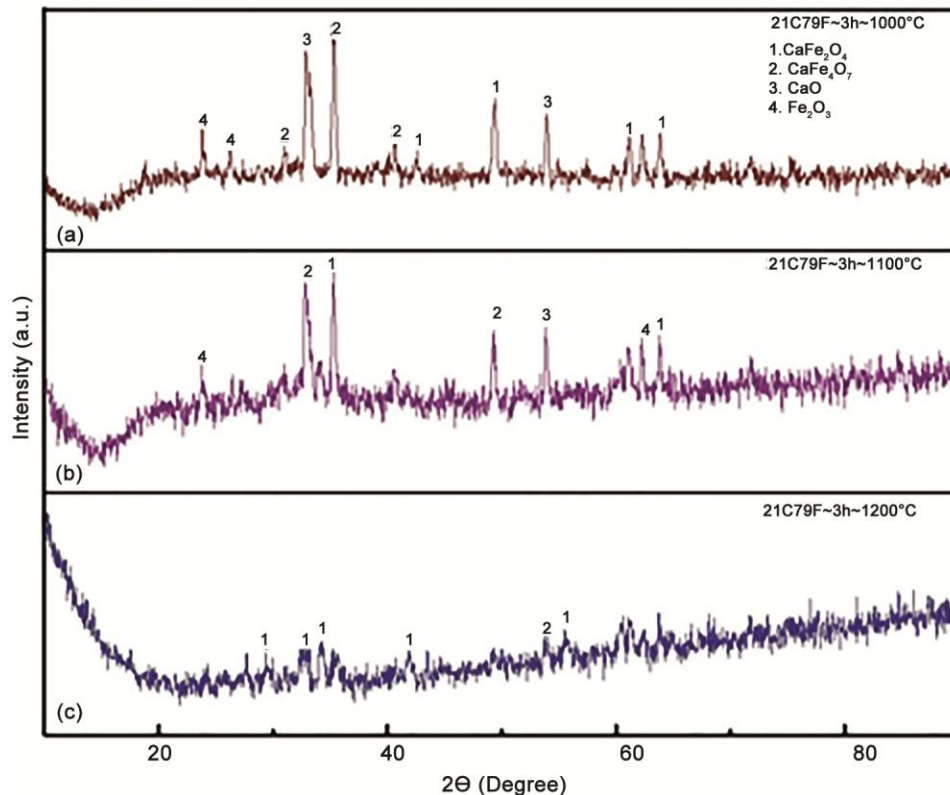

Fig. 9 — XRD pattern of heat treated CaO-Fe₂O₃ at different temperature for three hours.
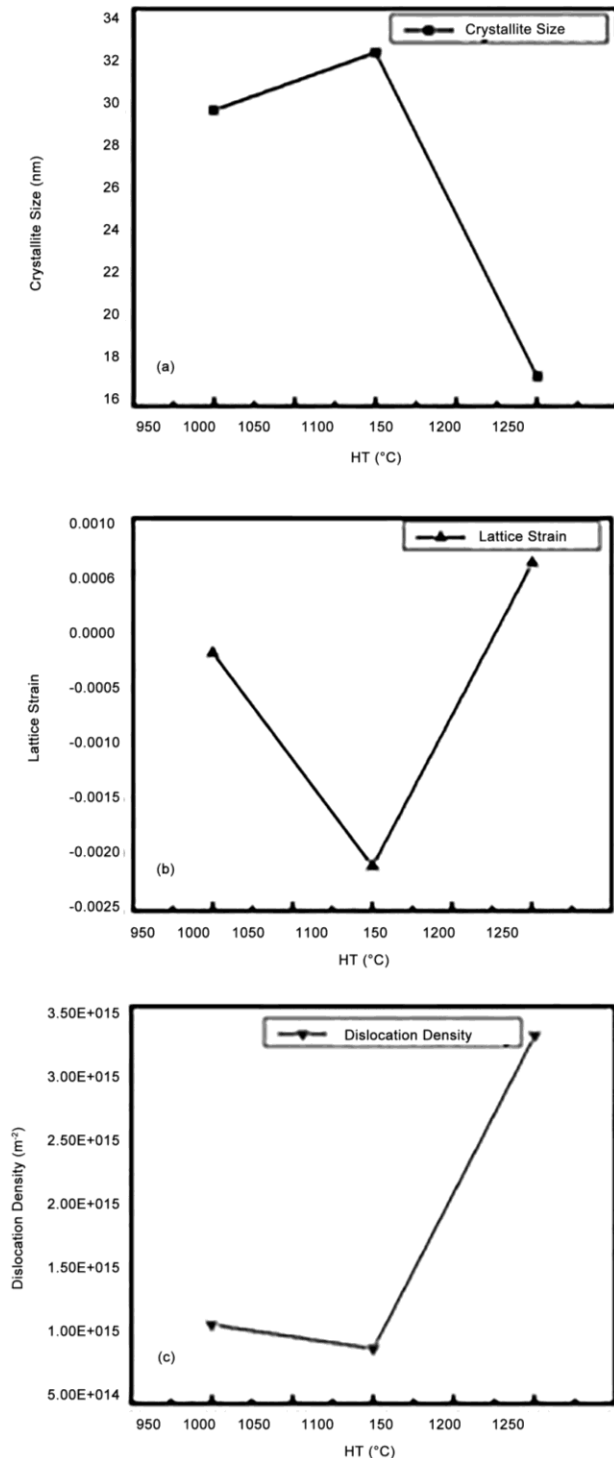
Fig. 10 — Effect of heating temperature (HT) on (a) crystallite size, (b) lattice strain, and (c) dislocation density.

4.3 Thermo gravimetric analysis (TGA) of CaO-Fe$_2$O$_3$ powder

Figure 11 shows the TGA curve of CaO-Fe$_2$O$_3$ heat-treated sample at different temperatures for 3 hours. The initial weight loss appeared at 480°C when the material was heated from room temperature. Due
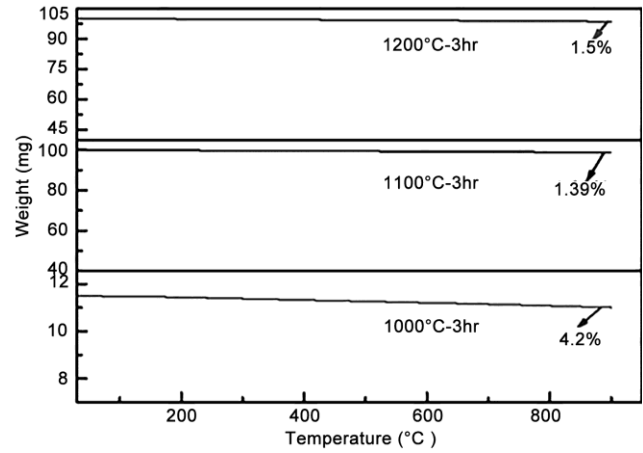

Fig. 11 — TGA curve of heat-treated sample (CaO-Fe$_2$O$_3$).

to the evaporation of volatile impurities, the rate of weight loss was very slow. When the sample was heat-treated at 1000°C, the high thermal stability and the weight loss were observed about 4.2% at 859°C. Furthermore, the graph indicates that high thermal stability and the weight loss observed about 1.39% at 899°C and 1.5% at 900°C subjected to heat treatment at 1100°C and 1200°C respectively. It has been noticed that there was no structural loss of CaO-Fe$_2$O$_3$ material because the weight loss was reported below 4.2% in all cases of the material.

4.4 Morphological study of CaO-Fe$_2$O$_3$ powder

The morphological studies have been carried out with FE-SEM of CaO-Fe$_2$O$_3$ (21:79 by wt. %). The image of sample powder before heat treatment is shown in Fig. 12 (a) and powder prepared from the heat-treated pellets at different heating temperatures (HT) for a constant soaking time of three hours as shown in Fig. 12 (b), (c), and (d). The grain size structure and elemental analysis of sample powder reveal the percentage of constituents in which % of C found maximum due to sample holder was layered with carbon tape which lowered down the % of other elements so it could be neglected. When the sample was initially heat-treated for 1000°C, a minor portion of the material recrystallized and the shape appeared like groundnuts since it is heat-treated below its melting point. Further, when the sample was put for heating at 1100°C, It reported that the grain size quietly increased and the major portion was recrystallized but the % of Iron (Fe) were reduced and oxygen increased due to the formation of other oxides. But when the material gets heat-treated at 1200°C, all materials get recrystallized and converted
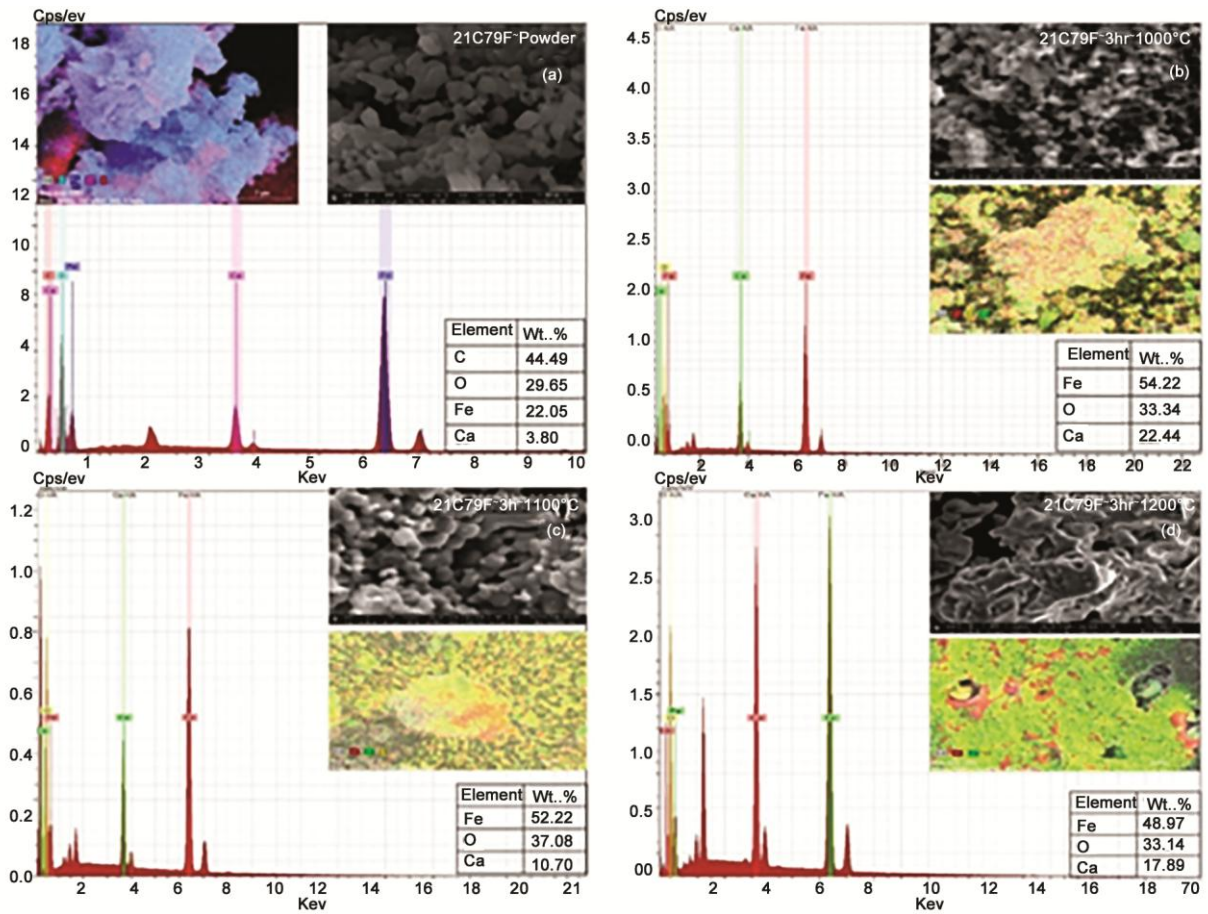
Fig. 12 — SEM image of CaO-Fe$_2$O$_3$ (21:79 by wt. %) powder with and without heat treatment.

into different oxides confirmed by XRD. As elemental analysis reported by EDS mapping in which fraction of Fe was reduced continuously but Ca increases at 1200°C due to the high melting point of CaO. Even the heating temperature was below its melting point (1220°C), still, the materials get recrystallized due to a high range of soaking time i.e. 3 hours. Recrystallization rate was found lower at 1000°C and 1100°C due to lower diffusion rate but at 1200°C all grains are restored and recrystallize due to high diffusion.

5 Conclusions

The studies of thermal stability, phase analysis, and morphology have been carried out of a sample material CaO-Fe$_2$O$_3$ (21:79 by wt. %) in the pellets form before and after heat treatment. The heat treatment process was carried out at 1000°C, 1100°C, and 1200°C for three hours soaking time. The powder of heat-treated pellets wascharacterized through XRD, DSC, and FE-SEM and the corresponding results have been discussed in the context of the heating

effect on phase analysis, thermal properties, and morphology. The values of specific heat and heat of fusion (enthalpy) both have been found maximum at 1100°C and then decreased with increasing the temperature but the crystallite size increased slightly and lattice strain decreased at this temperature. Here, the variation of thermophysical properties is very less hence this material can be used in molten form for further study of thermal diffusivity, thermal conductivity, and viscosity so that it can be compared with properties of corium for validation of simulant material for a nuclear reactor.

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