Microstructural Analysis of $CaO\text{-}Fe_2O_3$ Heat Treated at Different Temperature

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Abstract. In present paper a study has been carried out to analyze the thermophysical properties and microstructural behavior of $CaO.Fe_2O_3$.A binary eutectic sample material is taken in the ratio of 22:78 by wt. % in mixed powder form prepared manually. The sample powder is heat-treated at 950°C, 1050°C, and 1150°C for three hour holding time in programmable furnace. Further, the characterization is done with the help of different characterization technique like DSC, XRD, TGA to analyze its thermophysical properties and microstructural changes. This studies became necessary to analyze and interpret the data collected from prototype material found from nuclear severe accident occurred in the past. As heat transfer phenomena plays the crucial role in nuclear severe accident due to high temperature gradient developed inside the reactor vessel. Hence a non-prototype material is needed to study about heat transfer phenomena and in context of this study the material $CaO.Fe_2O_3$ is being considered. This study bears the first stage to validate the given material is simulant material. In the current study, heat absorbed, phase analysis, unit cell volume, melting point, crystallite size, dislocation density, and weight loss have been reported and analyzed.

Keywords: Nuclear Severe Accident, $CaO.Fe_2O_3$, Simulant Materials, Thermophysical Properties.

1. Introduction

Many severe accidents happened in nuclear reactor earlier reported by various researchers and accumulated the data for analysing the real issues occurred during accident scenarios. The analysis of thermophysical properties of prototype materials is necessary to investigate the real problems of severe accidents. For these purpose, there are various non-prototype materials have been used by researchers like $CaO\text{-}B_2O_3$, $CaO\text{-}SiO_2$, $WO_3\text{-}CaO$, $WO_3\text{-}Bi_2O_3$, $Mn\text{-}TiO_2$, $BiO_3\text{-}TiO_2$ etc. due to certain limitations of prototype materials. Shakov et. al studied on corium ingot and found that it is formed by mixing of liquid UO_2 and liquid steel [1]. Ding C et al reported during effect of cooling rates on the crystallization phase that the activation energy of $CaO\text{-}Fe_2O_3$ is -172.61 kJ/mole [2].The thermal stability of non-prototype material is needed for study and analysis of severe accident phenomena because the physical

properties should have similar tendency to mitigate the real problems. As heat transfer is key issue in nuclear power plant (NPP) for accountability of accident in reactors especially water cooled reactors due to high thermal gradient established inside it. Hence material should be thermally stable and eco-friendly for human beings. Li Y et al investigated the physical properties and microstructure of ceramics with various proportion of Fe_2O_3 and found that it not act as a flux but also enhance the crystal formation tendency [3].Ghosh A et. al devoted his effort to find the microstructure of CaO-Fe_2O_3 during sintering of lime along with Fe_2O_3 that the grain structure of CaO is spherical and when added to Fe_2O_3 its grain size increases [4].Another well-known experimental program conducted by Karabojian et. al named DEFOR TEST in which WO_3-CaO simulant material was used to find the debris behaviour in hypothetical reactor [5].A binary mixture of CaO-B_2O_3 was used as a simulant material in RIT experiment to report the fact of quenching phenomena and uniform porosity in melted material popularly known as DECOBI [6].In current research work an attempt has been taken to validate the CaO-Fe_2O_3 as simulant material whose thermophysical properties are analysed through various characterization techniques and could be supportive to study the actual phenomena occurred in corium melt during severe accident of nuclear reactor. The task accomplished by using mixed powder of CaO and Fe_2O_3 in a fixed ratio 22:78 by wt. % and heat-treated at 950°C, 1050°C, and1150°C for 3 hours holding time in a programmable furnace. This work reveals the information about enthalpy, unit cell volume, crystallite size, dislocation density, specific heat, thermal diffusivity.

2. Materials and Methodology

A eutectic binary ratio is being taken for analysis of microstructural and physical behavior of CaO and Fe_2O_3 in the ratio of 22:78 by weight % confirmed by phase diagram [7]. The material is prepared manually in mortar for 40 minutes and corresponding samples were formed for investigation. The characterization of CaO-Fe_2O_3 have been carried out with the help of different characterization technique like XRD (X-ray diffraction), DSC (Differential scanning calorimetry) and TGA (Thermogravimerty analysis). After characterization the analysis of thermo-physical properties along with microstructural behavior are being carried out accordingly. A subsubsection. The paragraph text follows on from the subsubsection heading but should not be in italic.

3. Results and Discussion

DSC plot of heat treated CaO-Fe_2O_3 has been shown in Fig: 1.The material is heat treated at 950°C, 1050°C and 1150°C, for holding time three hours. There are different endothermic peaks are shown in which the melting points appeared at corresponding heating temperature when the materials are thermally interacted at different temperature. The first peak appeared at 1196°C where phase transition occurred initially and completely melt at 1217°C when sample was hold for three hours at 950°C. Another endothermic peak was found at 1212°C when heat treated material at temperature 1050°C kept for three hours, material melted completely. Finally, when the sample is heat treated at 1150°C for three hours it indicates the endothermic peak at 1213°C where material turned into liquid state completely. The melting point of CaO-Fe_2O_3 do not differ significantly after heat treated at 950°C, 1050°C and,1150°C for three hours which indicates the thermal stability of material. The heat of fusion (Enthalpy) was found maximum at 1150°C as shown in Table1.

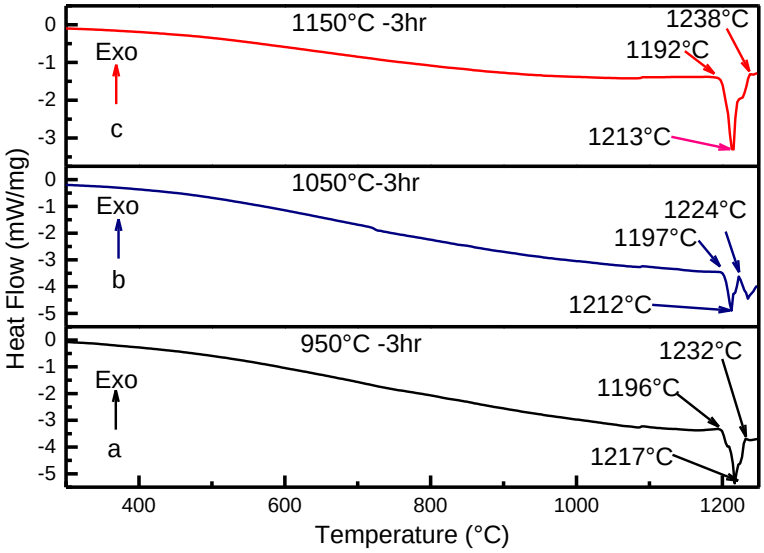

Figure 1**:** DSC Plot of sample CaO-Fe_2O_3 heat treated at 950°C, 1050°C and 1150°C for 3hr.

Table 1: Comparisons of Heat of Fusion, Melting point with different temperature and time

S.No.	Temperature (T)	Holding time (t)	Heat of Fusion (H_m)	Melting point (Tm)
3	950°C	3hr	145.3 J/g	1219°C
6	1050°C	3hr	68.67, 50.48 J/g	1212°C,1234°C
9	1150°C	3hr	185.9 J/g	1212°C

The phase analysis of heat treated material CaO-Fe_2O_3 has been studied with X-Ray diffraction thermogram shown in Fig.2. When Powder sample is heat treated at 950°C for three hour holding time, the values of 2θ with matching planes are given as 24.06°,(012); 31.93°,(230); 33.41°,(040); 33.57°,(320); 35.46°, (201); 40.28°,(131); 42.74°, (311); 46.59°,(250); 49.64°,(401) and 61.30°(170) shown in Fig. 2 (c). Further the powder sample of CaO-Fe_2O_3 is heat treated at 1050°C temperature for three hour holding time, the values of 2θ with matching planes are given as 33.73°, (320); 35.60°,(201); 40.46°, (131); 42.90°, (311); 49.89°,(401) and 61.41° (170) shown in Fig. 2 (b). After 3 hour heating, recrystallization continues and small grain obtained due to thermally rearrangement of crystal. Finally the sample was heat treated at 1150°C temperature for three hour holding time. The values of 2θ with matching planes are given as 25.49, (220); 31.95,(230); 32.98, (025);33.39°, (040); 33.58°,(320); 35.47° (201); 40.27°, (131); 42.71°, (311); 49.74°,(401) and 61.32° (170) as shown in Fig. 2 (a).

The following phases were found like Fe_2O_3, $CaFe_4O_7$, and $CaFe_2O_4$ during heat treatment of CaO-Fe_2O_3 at 950°C, 1050°C and 1150°C for three hours confirmed by XRD.The thermophysical properties are summarized in Table 2, unit cell volume and crystallite size increases with increasing temperature but the lattice strain and dislocation density decreases with increasing temperature. The crystal structure was found as orthorhombic when samples were heat treated at different temperature for constant holding time.

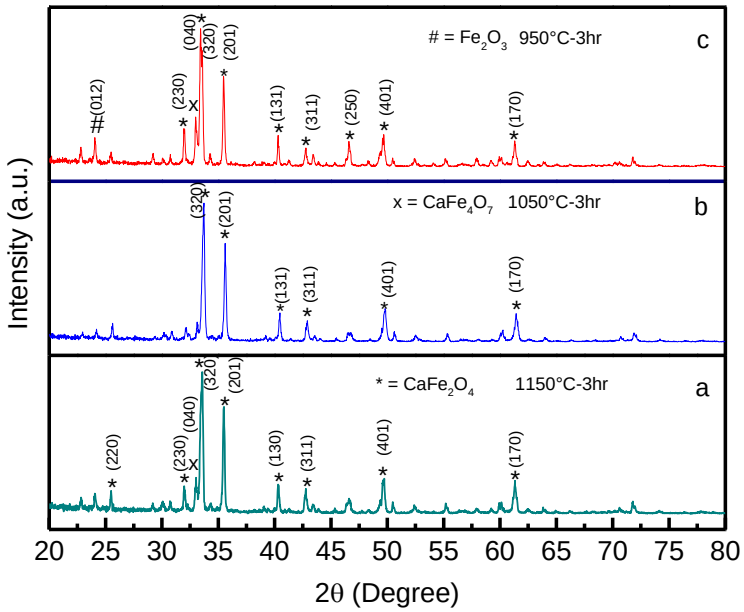

Figure 2**:** XRD plots with different temperature at fixed time 3hr

Table 2: Comparative values of lattice parameter, crystal structure and dislocation density.

S. No.	Temperature	Interplanar Distance, d_{hkl}(Å),& 2θ	Lattice Parameter (Å)	Crystal structure	Unit cell Volume (Å)	Crystallite size, d (nm)	Lattice strain 'ε'	Dislocation density, $1/d^2$ (m^{-2})
1	950°C, 3hr	2.679, 33.41°	a=9.245, b= 10.72, c = 2.87	orthorhombic	284	60	0.0021	$2.7x10^{14}$
2	1050°C,3hr	2.657, 33.73°	a = 9.20, b = 10.63, c = 3.01	orthorhombic	294	63	0.0020	$2.5x10^{14}$
3	1150°C,3hr	2.68, 33.58°	a= 9.19, b= 10.72, c= 3.03	orthorhombic	298.5	73	0.0017	$1.87x10^{14}$

The TGA thermogram depicts that the weight loss occurred during heat treatment of CaO-Fe_2O_3 at different temperature for three hours. Weight loss were found as 4.2%, 1.39% and 1.5% at 950°C, 1050°C and 1150°C respectively. Maximum weight loss occurred at 950°C initially due to presence of volatile material in the sample.

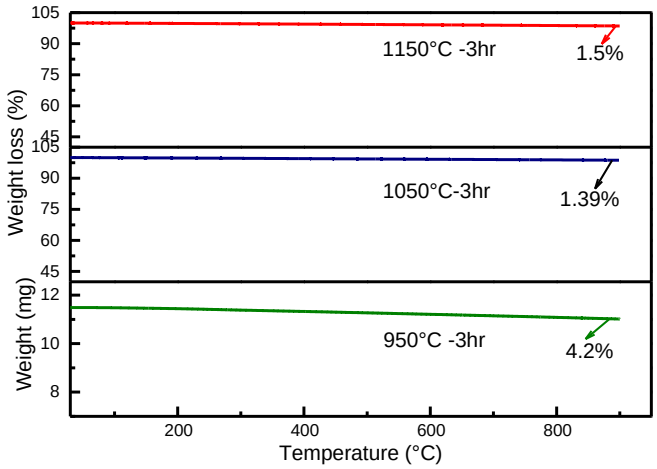

Figure 3: Weight loss of CaO-Fe_2O_3 heated at 950°C, 1050°C and 1150°C

4. Results and Discussion

Since there are various simulant materials have been used till date to understand the physical phenomena occurred during severe accident scenario. Another material CaO-Fe_2O_3 is being considered for current research work in which characterization has been carried out and studied. The task accomplished by using mixed powder of CaO and Fe_2O_3 in a fixed ratio 22:78 by wt. % and heat-treated at 950°C, 1050°C, and1150°C for 3 hours holding time in a programmable furnace. Initially it has been found that the material is thermally stable and further this work reveals the information about enthalpy, unit cell volume, crystallite size, dislocation density, specific heat, thermal diffusivity.

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