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THERMAL CHARACTERISATION OF CALCIUM FERRITES BY LASER FLASH METHOD

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The thermal constants, viz., thermal diffusivities, specific heat capacities and thermal conductivities of samples of mono- and di- calcium ferrites, prepared in the laboratory, have been obtained by laser flash method using an Ulvac-Sinku-Riko TC-3000 series instrument. The temperature range used was from 298–1100 K. All possible thermodynamic parameters associated with the heat capacity data were also calculated.

Introduction

The advent of nuclear fast reactors and controlled thermonuclear reactors has led to a growing interest in the chemistry of liquid metals and their corrosion products with the container materials. The corrosion of 300 series stainless steel or nickel base alloys in which the principal constituents are iron, chromium and nickel are of particular interest. These metals are sparingly soluble in liquid sodium and lithium and do not form any inter-metallic compounds. Contamination with oxygen can lead to the formation of double oxides of these elements. Though the formation of double oxides of Ni, Fe and Cr with Na and Li are more probable, the calcium impurity in liquid alkali metals can also form same type of double oxides.

In order to assess the corrosion reactions and the impact of the corrosion products on the heat transfer properties of liquid alkali metals, thermodynamic studies [1–4] of their double oxides were undertaken in this laboratory. The present work covers the measurement of specific heat

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capacities, thermal diffusivities and thermal conductivities of $CaFe_2O_4$ and $Ca_2Fe_2O_5$ by laser flash method and involves the calculation of some thermodynamic parameters of these double oxides.

These data will find their utility in ferrous industry as their compounds are of importance as slags and refractories in smelting processes [5, 6].

Experimental

The preparation of the compounds was based on the high temperature solid state reaction [7] of calcium carbonate with ferric oxide in the required ratio.

$$CaCO_3(S) + Fe_2O_3(S) \xrightarrow[24\,h]{1150^\circ C} CaFe_2O_4(S) + CO_2(g)$$

$$2CaCO_3(S) + Fe_2O_3(S) \xrightarrow[24\,h]{1150^\circ C} Ca_2Fe_2O_5(S) + CO_2(g)$$

As some oxygen deficiency was noticed in the compounds, a slow dynamic oxygen atmosphere was maintained for the preparations.

The stoichiometry and the composition of the compounds were confirmed by chemical analysis as well as X-ray diffraction methods. A recheck was done on the chemical analysis by atomic absorption spectrophotometry.

For the measurement of the thermal constants an Ulvac-Sinku-Riko Model TC 3000-H instrument which employs a laser flash technique, was used. The technique of preparation of the pellets for study, the measurement of actual densities and the experimental procedure have already been published in an earlier publication of the authors [4]. The temperature range of measurement was 298–1100 K. Saphire was used as the reference. The error involved was less than 3%.

Results and discussion

The time $t_{1/2}$ required to raise the temperature of the sample to half the maximum temperature and the maximum temperature attained T_{max} were obtained as a function of temperature in the range of 298 –1100 K and these parameters were utilised to get the thermal diffusivities and the specific heat capacities respectively using the appropriate equations [4]. The product of thermal diffusivity, specific heat capacity and the actual density gave the thermal conductivity at any given temperature. These data were fitted into appropriate polynomial equation and the three thermal constants viz. thermal diffusivity, specific heat capacity and thermal conductivity at various temperatures, were computed. The data on $CaFe_2O_4$ and $Ca_2Fe_2O_5$ are listed in Tables 1 and 2.

Table 1 Thermal constants measurements of $CaFe_2O_4$

Temperature, K	Thermal diffusivity, $\alpha \times 10^3$ cm^2 sec^{-1}	Specific heat, J.K.$^{-1}$g^{-1}	Thermal conductivity, W m^{-1}K^{-1}
297	4.384	0.710	1.525
375	3.302	0.815	1.319
423	2.641	0.916	1.185
483	2.483	1.011	1.237
555	2.672	1.015	1.329
627	2.501	1.020	1.310
717	2.340	1.092	1.252
886	2.480	1.091	1.327
987	2.501	1.095	1.342
1091	2.520	1.100	1.358

Table 2 Thermal constants measurements of $Ca_2Fe_2O_5$

Temperature, K	Thermal diffusivity, $\alpha \times 10^3$ cm^2 sec^{-1}	Specific heat, J.K.$^{-1}$g^{-1}	Thermal conductivity, W m^{-1}K^{-1}
296	9.396	0.661	2.832
361	8.223	0.726	2.722
431	7.149	0.810	2.641
495	6.347	0.828	2.396
555	5.856	0.877	2.342
628	5.477	0.888	2.218
682	5.312	0.893	2.163
778	5.195	0.893	2.115
886	5.269	0.900	2.162
986	5.426	0.906	2.241
1090	5.566	0.941	2.388

The specific heat capacity data were further used to calculate the thermodynamic parameters, viz. the enthalpy increments, $H_T^0 - H_{298}^0$, the entropy increments, $S_T^0 - S_{298}^0$ and the free energy increments,$G_T^0 - G_{298}^0$ at various temperatures.

These parameters for $CaFe_2O_4$ and $Ca_2Fe_2O_5$ are presented in Tables 3 and 4 respectively.

Table 3 Thermodynamic parameters of $CaFe_2O_4$

Temperature, K	$H_T^0 - H_{298}^0$, kJ. mole^{-1}	$S_T^0 - S_{298}^0$, J.K^{-1}g^{-1}	$-(G_T^0 - G_{298}^0)$, kJ. mole^{-1}
400	17.26	0.231	2.67
500	37.70	0.442	9.97
600	60.05	0.632	21.74
700	83.28	0.800	37.51
800	106.79	0.946	56.45
900	130.24	1.074	78.26
1000	153.60	1.188	102.65
1100	177.20	1.289	128.64

Table 4 Thermodynamic parameters of $Ca_2Fe_2O_5$

Temperature, K	$H_T^0 - H_{298}^0$, kJ. mole^{-1}	$S_T^0 - S_{298}^0$, J.K^{-1}g^{-1}	$-(G_T^0 - G_{298}^0)$, kJ. mole^{-1}
400	19.54	0.208	3.07
500	41.45	0.385	10.87
600	64.80	0.541	23.43
700	88.93	0.678	40.06
800	113.39	0.799	60.34
900	137.88	0.905	83.50
1000	162.45	1.000	109.35
1100	187.19	1.087	137.80

The change in the three thermal constants with temperature is more or less monotonic. For the compound with high stoichiometry, the values of thermal diffusivity and thermal conductivity are much higher as expected. But the specific heat values are found to be smaller in magnitude. The averaging of the temperature for the calculation of the thermodynamic parameters has yielded a monotonic increase as expected.

Figures 1 and 2 depict the change in the specific heats of $CaFe_2O_4$ and $Ca_2Fe_2O_5$ against temperature. As can be seen from the figures, in the case of $Ca_2Fe_2O_5$ our values are in general agreement with the measurements of

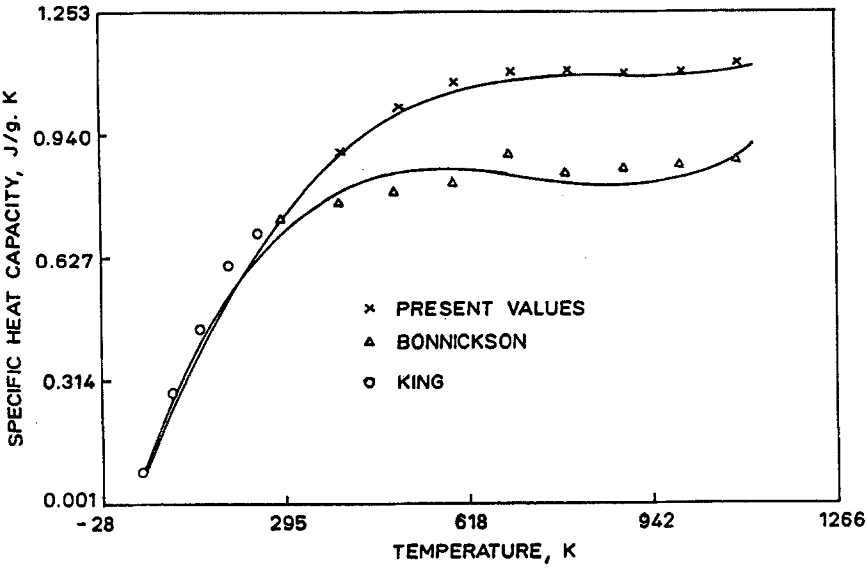

Fig. 1 Specific heats of Ca Fe_2O_4 *vs.* *T*

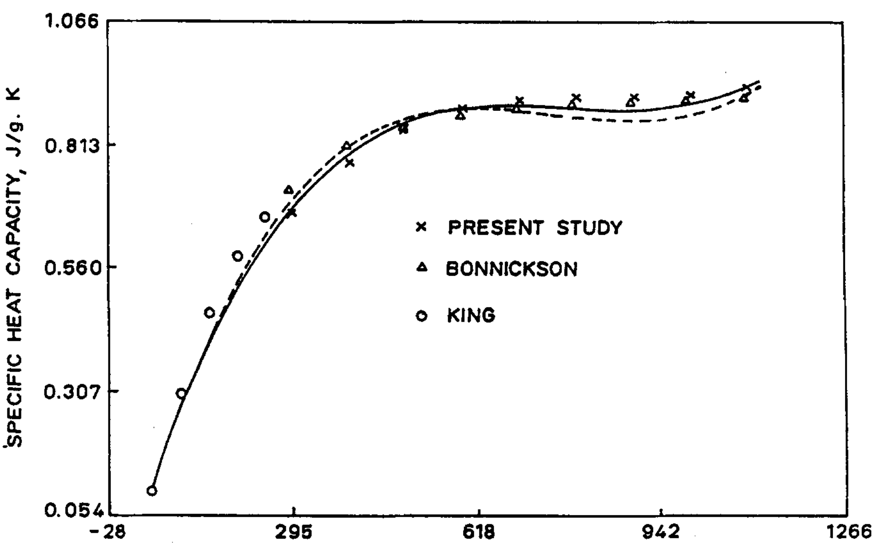

Fig. 2 Specific heats of $Ca_2Fe_2O_5$ *vs.* *T*

Bonnickson [8] by drop method. But The values for $CaFe_2O_4$ are on the higher side. King [9] has determined the specific heat capacities of these compounds in the temperature range of 51–298 K by drop method and his data curves coalese smoothly with the curves of the present work.

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Zusammenfassung — Mittels Laser Flash Verfahren wurden unter Zuhilfenahme eines Instrumentes der Serie Ulvac-Sinku-Riko TC-3000 die thermischen Konstanten, d.h. die Temperaturleitzahl, die spezifischen Wärmekapazität und die Wärmeleitzahl von in unserem Labor hergestellten Mono- und Dicalciumferriten bestimmt. Der verwendete Temperaturbereich erstreckte sich von 298 bis 1100 K. Alle mit der Wärmekapazität verbundenen thermodynamischen Parameter wurden ebenfalls berechnet.