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SOLID–SOLID INTERACTION BETWEEN FERRIC OXIDE AND SODIUM NITRATE AND THERMAL STABILITY OF THE SODIUM FERRITES PRODUCED

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ABSTRACT

The interaction between α-Fe_2O_3 and $NaNO_3$ was studied using DTA, TG, DTG and X-ray diffraction techniques

The results obtained revealed that ferric oxide prevented the thermal decomposition of sodium nitrate, even when heated for a long period at 500 °C, owing to the formation of some type of solid solution of Fe_2O_3 in the molten $NaNO_3$ When these solids were mixed in equimolar ratios they underwent solid–solid interaction at 700 °C yielding well-crystallized $NaFeO_2$(tetragonal) and α-$NaFeO_2$(hexagonal) phases Heating at 800 °C resulted in the thermal decomposition of most of the $NaFeO_2$ produced and led to the formation of a small amount of β-$NaFeO_2$ without affecting the crystallinity of the α-$NaFeO_2$ The α- and β-$NaFeO_2$ phases disappeared on heating at 900 °C, while well-crystallized $NaFeO_2$(tetragonal) and $Na_{10}Fe_{16}O_{29}$ phases appeared Heating at 1000 °C brought about a complete conversion of $NaFeO_2$ into well-crystallized $Na_{10}Fe_{16}O_{29}$, which decomposed completely at 1100 °C giving α-Fe_2O_3 and $NaFeO_2$(tetragonal) However, the ferrite produced suffered some type of deformation

Similar results were obtained for Fe_2O_3 and $NaNO_3$ mixed in a molar ratio of 2 1, however, β-$NaFeO_2$ was not produced and $Na_{10}Fe_{16}O_{29}$ was stable even when heated at 1100 °C

INTRODUCTION

Sodium ferrite exists in two stable forms having the formulae $NaFeO_2$ and $Na_{10}Fe_{16}O_{29}$ [1–5] The former compound exists in three different crystallographic forms α, β and γ [1,3,4] Alpha-$NaFeO_2$ can be prepared by an interaction between α-Fe_2O_3 and molten NaOH at about 200 °C in an inert atmosphere, or via solid–solid interaction between α-Fe_2o_3 and Na_2CO_3 at temperatures between 500 and 700 °C Sodium ferrite, $Na_{10}Fe_{16}O_{29}$, can be obtained by the interaction between $NaFeO_2$ and ferric oxide at 850 °C [3,4] The preparation and physicochemical, magnetic and structural characterization of sodium ferrites have been the object of several investigations [3,4,6–10] However, the various factors affecting the thermal stability of sodium ferrites have received less attention

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This paper reports the results of a study on the solid–solid interactions between Fe_2O_3 and $NaNO_3$ (molar ratios 1 1 and 2 1) and on the thermal stability of the sodium ferrites produced The techniques employed were DTA, TG, DTG and X-ray diffraction

EXPERIMENTAL

Materials

Two specimens of ferric oxide and sodium nitrate were prepared by mixing finely powdered, well-crystallized, α-Fe_2O_3 with $NaNO_3$ with the addition of a small amount of distilled water The Fe_2O_3 $NaNO_3$ molar ratios were 1 1 and 2 1 The solid samples produced were dried at 100 °C and calcined in air at temperatures between 500 and 1100 °C, the time of heating was fixed at 6 h

Techniques

DTA, TG and DTG analyses of the two Fe_2O_3–$NaNO_3$ specimens were carried out using a Netzsch–Geratebau simultaneous thermal analysis apparatus (STA 409, type 6 223) The rate of heating was 10 °C min^{-1} and 200 mg of each specimen was used

An X-ray investigation of the thermal products of the solids was performed with a Philips diffractometer (type PW 1390) The patterns were run with iron-filtered Co radiation ($\lambda = 1\ 7889$ Å) at 40 kV and 30 mA with a scanning speed of 2° in 2θ min^{-1}

RESULTS AND DISCUSSION

Thermal behaviour of Fe_2O_3–$NaNO_3$ solids

Figures 1 and 2 show DTA, TG and DTG curves of mixtures of ferric oxide and sodium nitrate (molar ratios of 1 1 and 2 1) Two strong, sharp endothermic peaks are observed for both samples The maxima of these peaks are located at 310 and 734 °C for the sample with a molar ratio of 1 1 and at 280 and 710 °C for the sample with a molar ratio of 2 1 The peaks at 280 and 310 °C are not accompanied by any loss in weight, whereas the peaks at 710 and 734 °C are followed by 14% and 23% loss in weight for the solids having the compositions $2Fe_2O_3$ $NaNO_3$ and Fe_2O_3 $NaNO_3$, respectively The peaks at 280 and 310 °C may characterize a phase transformation rather than a chemical interaction In fact pure sodium nitrate melts at 306 8 °C and decomposes at 380 °C [11] These peaks thus correspond to the

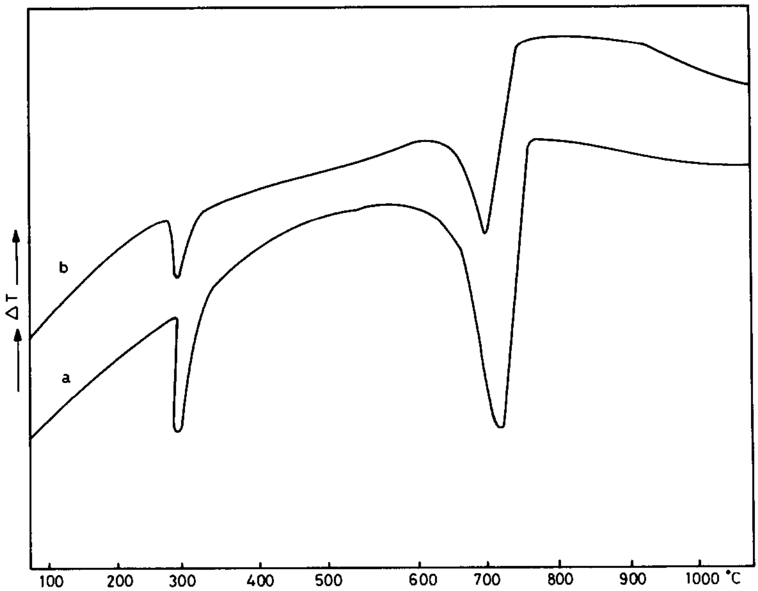

Fig 1 DTA curves of mixtures of solids of ferric oxide and sodium nitrate with the compositions (a) Fe_2O_3 $NaNO_3$ and (b) $2Fe_2O_3$ $NaNO_3$

change $NaNO_3(s) \rightarrow NaNO_3(l)$ The absence of any endothermic peak in the DTA curves (Fig 1) at temperatures near the normal decomposition temperature of sodium nitrate clearly indicate the role of Fe_2O_3 in hindering the thermal decomposition of the molten $NaNO_3$ The peaks at 710 and 734 °C may correspond to solid–solid interaction between ferric oxide and sodium nitrate, producing sodium ferrite compound(s). In fact, it has been reported by Neroslavskaya et al [9] that Fe_2O_3 interacted with Na_2CO_3 at 700 °C to produce sodium ferrite, $NaFeO_2$ The identification of the sodium ferrite compounds formed at the different temperatures was performed using XRD measurements (see below)

X-ray investigation of the thermal products of ferric oxide and $NaNO_3$

XRD revealed that the ferric oxide employed consisted entirely of the well-crystallized α-Fe_2O_3 phase. Figures 3 and 4 represent the X-ray diffraction patterns of the Fe_2O_3 $NaNO_3$ and $2Fe_2O_3$ $NaNO_3$ samples, respectively, precalcined for 6 h at 500, 700, 800, 900, 1000 and 1100 °C Additional samples were subjected to prolonged heating for 24 h at 500 °C It can be seen from Figs. 3 and 4 that all the diffraction lines of the α-Fe_2O_3 and $NaNO_3$ phases were detected in the patterns of the samples precalcined at 500 °C for 6 h and 24 h These results clearly indicate the effect of Fe_2O_3 in preventing the thermal decomposition of the molten $NaNO_3$ even when heated at 500 °C for a long period, and also show the absence of any

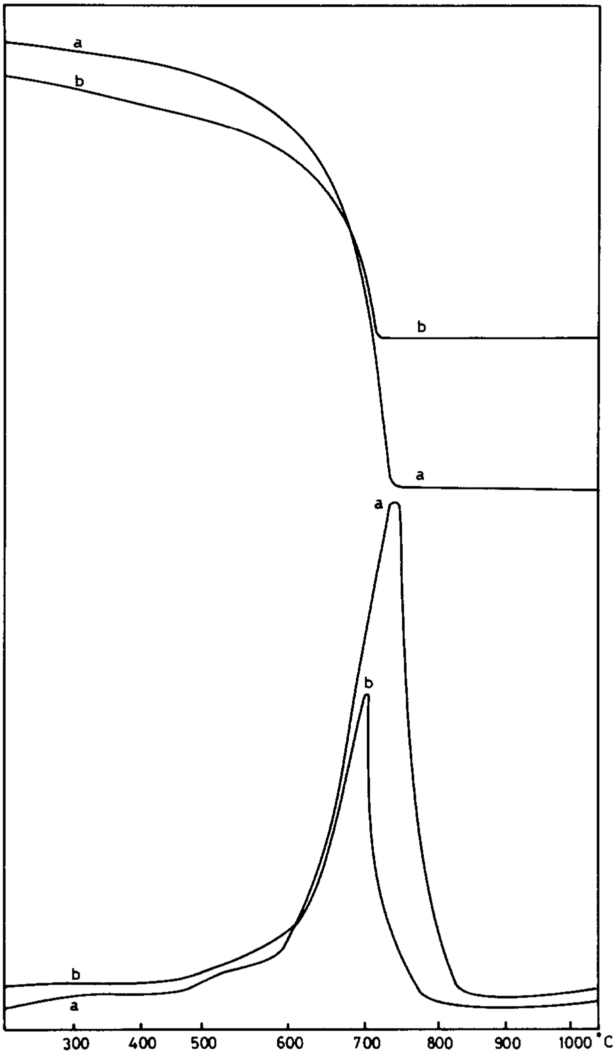

Fig 2 TG and DTG curves of mixtures of solids of ferric oxide and sodium nitrate with the compositions (a) Fe_2O_3 $NaNO_3$ and (b) $2Fe_2O_3$ $NaNO_3$

chemical interaction between these solids at this temperature The acquired thermal stability of sodium nitrate in the presence of ferric oxide may be tentatively attributed to the possible formation of some type of solid solution of Fe_2O_3 in the molten $NaNO_3$ The absence of any solid–solid interaction at 500 °C is not surprising In fact, it has been reported by several workers that the solid–solid interaction between α-Fe_2O_3 and Na_2CO_3 does not take place at temperatures below 700 °C [7,9] However, Thery and Collongues [3,4] have reported a possible chemical interaction, in the solid state, between γ-Fe_2O_3 and Na_2CO_3 producing sodium ferrites at temperatures starting from 500 °C

Heating the samples at 700 °C led to the disappearance of all the diffraction lines of the free $NaNO_3$ phase (cf. Figs. 3 and 4) and a subsequent appearance of two sets of diffraction lines The diffraction lines of α-Fe_2O_3 were detected in the patterns of the various samples precalcined at 500–1100 °C These lines are not given in Figs. 3 and 4 with the exception of the solids precalcined at 500 °C. The *d* spacings of the newly detected lines were calculated to be 2 64, 4 $30_{0\,8}$, 3 $02_{0\,7}$, $4.45_{0\,65}$, 2 $84_{0\,50}$ and 2 19_x, $5.37_{0\,7}$, $2.49_{0\,5}$, $1.51_{0\,4}$. These lines characterized two sodium ferrite phases, namely $NaFeO_2$(tetragonal) and α-$NaFeO_2$(hexagonal), respectively [12]. The intensities of the diffraction lines of the tetragonal form were almost

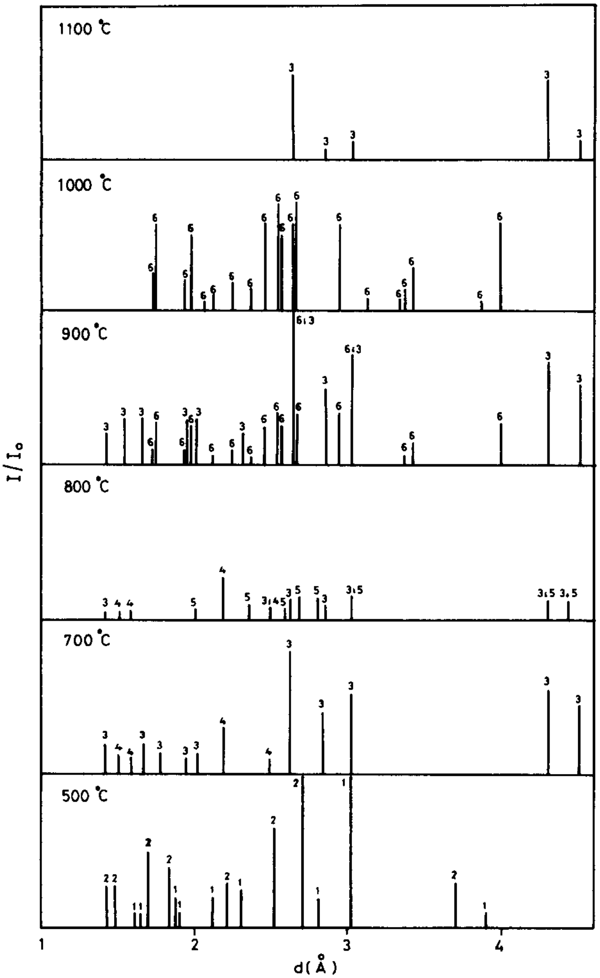

Fig 3 X-ray diffraction patterns of the thermal products of the solid Fe_2O_3 $NaNO_3$ (1) $NaNO_3$, (2) α-Fe_2O_3, (3) $NaFeO_2$(tetragonal), (4) α-$NaFeO_2$, (5) β-$NaFeO_2$(hexagonal), (6) $Na_{10}Fe_{16}O_{29}$

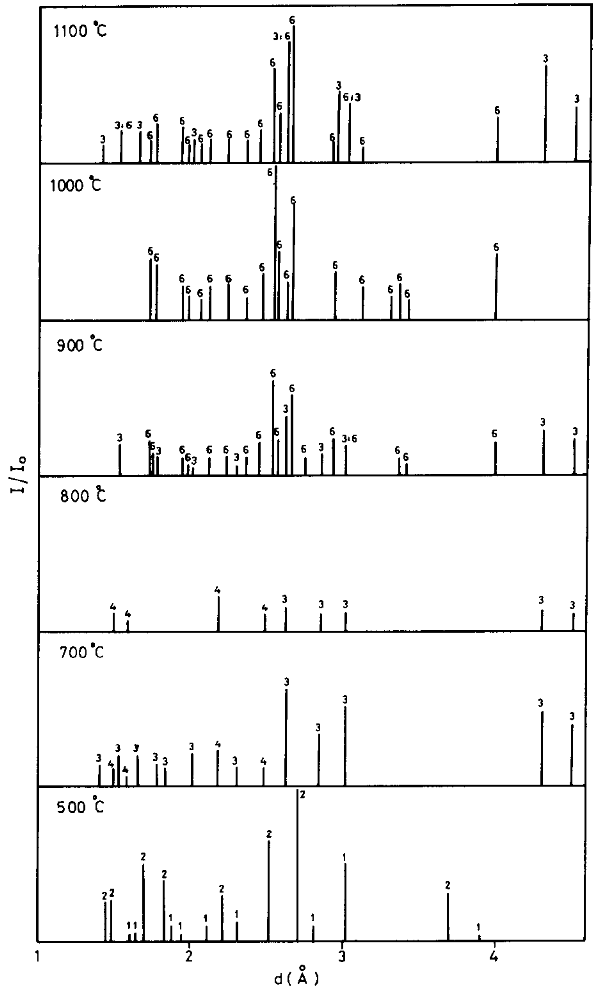

Fig 4 X-ray diffraction patterns of the thermal products of the solid $2Fe_2O_3$ $NaNO_3$ (1) $NaNO_3$, (2) α-Fe_2O_3, (3) $NaFeO_2$, (4) α-$NaFeO_2$, (5) β-$NaFeO_2$, (6) $Na_{10}Fe_{16}O_{29}$

twice those of the hexagonal form The formation of these compounds may proceed according to the reaction

$$3Fe_2O_3 + 6NaNO_3 \xrightarrow{700\,^\circ C} 4NaFeO_2(\text{tetragonal}) + 2NaFeO_2(\text{hexagonal}) + 6NO_2(g) + 3/2O_2(g)$$

The completion of this reaction, in the samples with the compositions Fe_2O_3 $NaNO_3$ and $2FeO_3$ $NaNO_3$ should be followed by a loss in weight of 22 and 12 5%, respectively. These values are very close to those found experimentally (cf Fig 2), indicating the absence of any unreacted $NaNO_3$ This conclusion agrees well with the XRD measurements

It can be seen from Figs 3 and 4 that an increase in the precalcination temperature to 800 °C results in a considerable decrease (about 80%) in the crystallinity of NaFeO(tetragonal), without affecting the crystallinity of α-$NaFeO_2$(hexagonal). These results indicate the thermal stability of the α-phase at 800 °C and show the transformation of the majority of the tetragonal $NaFeO_2$ into a poorly crystalline compound Some of the diffraction lines, of very low intensity, characterizing β-$NaFeO_2$ [13] were also found in the diffraction patterns of Fe_2O_3 $NaNO_3$ preheated at 800 °C The formation of $NaFeO_2$(orthorhombic) occurred via transformation of a very small amount of $NaFeO_2$(tetragonal) Babcock-Hitachi [7] reported the formation of β-$NaFeO_2$ via an interaction between a black liquor (rich in NaOH) and powdered Fe_2O_3 in a fluidized bed furnace at 800 °C

It can also be seen from Figs 3 and 4 that a further increase in the precalcination temperature to 900 °C produces the disappearance of both α- and β-$NaFeO_3$ with the recrystallization of $NaFeO_2$ in the tetragonal form. This treatment also led to the appearance of all the diffraction lines of well-crystallized $Na_{10}Fe_{16}O_{29}$ These results enable us to write

$$NaFeO_2(\text{amorphous}) \xrightarrow{900\,^{\circ}C} NaFeO_2(\text{tetragonal})$$

$$10NaFeO_2(\text{tetragonal}) + 3Fe_2O_3 \xrightarrow{900\,^{\circ}C} Na_{10}Fe_{16}O_{29}$$

$$10NaFeO_2(\alpha \text{ and } \beta) + 3Fe_2O_3 \xrightarrow{900\,^{\circ}C} Na_{10}Fe_{16}O_{29}$$

These reactions are not accompanied by a loss or gain in weight of the reacting species, in accordance with the TG and DTG results (Fig 2) The fact that more of the DTA curves of the various samples include any endothermic or exothermic peaks at temperatures near 900 °C may indicate that the above-mentioned reactions take place very slowly at 900 °C and/or the thermal effects accompanying the reaction are too small to be easily detected The presence of a well-crystallized unreacted portion of $NaFeO_2$-(tetragonal) phase with the $Na_{10}Fe_{16}O_{29}$ phase in the samples precalcined for 6 h at 900 °C may indicate that the reactions leading to the formation of $Na_{10}Fe_{16}O_{29}$ take place slowly at 900 °C The completion of these reactions required prolonged heating at 900 °C or roasting at higher temperatures (1000 °C) In fact, the precalcination at 1000 °C of Fe_2O_3 and $NaNO_3$ mixed in molar ratios of 1 1 and 2 1 resulted in a complete transformation of $NaFeO_2$ into well-crystallized $Na_{10}Fe_{16}O_{29}$ as shown from Figs 3 and 4

It can also be observed from Figs 3 and 4 that the firing of the different samples at 1100 °C resulted in a complete decomposition of $Na_{10}Fe_{16}O_{29}$, in the case of the sample with an equimolar ratio of α-Fe_2O_3 and $NaNO_3$, producing well-crystallized α-ferric oxide and $NaFeO_2$(tetragonal) However, the relative intensities of most of the diffraction lines of $NaFeO_2$ produced at 1100 °C were effectively diminished (cf Fig 3) These results may indicate some type of deformation or disordering of the $NaFeO_2$ lattice In contrast, for the sample with a composition of $2Fe_2O_3$ $NaNO_3$, the sodium ferrite, $Na_{10}Fe_{16}O_{29}$, underwent partial thermal decomposition by firing at elevated temperatures (1100 °C) (Fig 4) These results indicate the role of excess Fe_2O_3 in increasing the thermal stability of $Na_{10}Fe_{16}O_{29}$ It seems that the presence of excess Fe_2O_3, more than twice the amount required for the formation of ferrite, shifts the reaction $Na_{10}Fe_{16}O_{29} \overset{1100\,^{\circ}C}{\rightleftharpoons} 10NaFeO_2 + 3Fe_2O_3$ in the reverse direction

CONCLUSIONS

The main conclusions that can be derived from the experimental results are as follows

(1) Ferric oxide mixed with sodium nitrate in molar ratios of 1 1 or 2 1 prevented the thermal decomposition of $NaNO_3$ even when heated for a long period at 500 °C Pure $NaNO_3$ decomposes readily at 380 °C The induced thermal stability of this compound may result from the formation of some type of solid solution of Fe_2O_3 in molten $NaNO_3$

(2) Solid–solid interactions between α-Fe_2O_3 and $NaNO_3$ occurred at 700 °C leading to the production of well-crystallized sodium ferrites $NaFeO_2$ (tetragonal and hexagonal forms) Most of the tetragonal form decomposed at 800 °C yielding amorphous compound(s) together with a small amount of β-$NaFeO_2$(orthorhombic)

(3) Alpha-Fe_2O_3 interacted with $NaFeO_2$ at 900 °C producing well-crystallized $Na_{10}Fe_{16}O_{29}$ which remained stable at 1000 °C This compound decomposed readily at 1100 °C in the sample containing an equimolar ratio of Fe_2O_3 and $NaNO_3$ However, an important increase in the thermal stability of $Na_{10}Fe_{16}O_{29}$ was observed for the sample with the composition $2Fe_2O_3$ $NaNO_3$

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