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SOLID-SOLID INTERACTIONS BETWEEN FERRIC OXIDE AND LITHIUM CARBONATE AND THE THERMAL STABILITY OF THE LITHIUM FERRITES PRODUCED

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ABSTRACT

The interaction between α-Fe_2O_3 and Li_2CO_3 was studied using DTA, TG DTG and X-ray diffraction techniques.

The results obtained revealed that ferric oxide and lithium carbonate, when mixed in a molar ratio of 1 : 2, underwent solid–solid interaction at temperatures starting from 500 ° C, yielding α-$LiFeO_2$. The degree of crystallinity of the ferrite produced was much increased by increasing the precalcination temperature of the mixed solids. The unreacted portion of lithium carbonate decomposed readily at 735 ° C forming Li_2O which dissolved in the α-$LiFeO_2$ lattice, giving a stable solid solution. The dissolved lithium oxide increased the thermal stability of α-$LiFeO_2$ and prevented its phase transformation into any other type of lithium ferrite. The heating of the mixed solids at 1080 ° C resulted in sublimation of about 50% of the Li_2O from the lattice of $LiFeO_2$ without effecting its transformation into another phase.

However, Fe_2O_3 and Li_2CO_3, in an equimolar ratio, interacted with each other at temperatures starting from 500 ° C also giving α-$LiFeO_2$ which was transformed in part into β-$LiFeO_2$ and β-$LiFe_5O_8$ at temperatures between 700 and 1000 ° C. At 1100 ° C, the β lithium ferrites and an important portion of α-$LiFeO_2$ underwent phase transformation forming well-crystallized α-$LiFe_5O_8$.

INTRODUCTION

Most monovalent ferrites exist in two forms, the first having the formula $Fe_2O_3 \cdot M_2O$ is cubic, rhombic or orthorhombic and the second having the composition $5Fe_2O_3 \cdot M_2O$ is cubic spinel [1]. The alkali ferrites of Li, Na, K, Rb and Cs represent one of the two categories of monovalent ferrites.

The alkali ferrites can be prepared by electrochemical methods [2,3] and by heating, at different temperatures in air or in an inert atmosphere, a mixture containing Fe_2O_3 and alkali oxides or carbonates [1,4–9].

Lithium ferrite, $LiFeO_2$, can be obtained by the thermal treatment, in air at 700 ° C, of mixed solids with equimolar proportions of Fe_2O_3 and Li_2O or Li_2CO_3 [4,6,8]. The solid obtained exhibits antiferromagnetic properties and acquires a cubic FeO structure on heating above 700 ° C followed by rapid

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cooling to room temperature [1]. Lithium and ferric cations of $LiFeO_2$ could be substituted, in part, with other cations such as Al^{3+} and Mn^{2+} forming various solid solutions [1,10].

Lithium ferrite, $LiFe_5O_8$, could be prepared by heating, at 400–1200 ° C, a powdered mixture containing Fe_2O_3 and Li_2CO_3 in a molar ratio of 5 : 1 [6,9]. The ferritization process starts at 450 ° C and reaches completion at 800 ° C [6]. Some physicochemical and magnetic properties of ferrites, such as lattice parameter, shrinkage, density, thermal stability, curie temperature and saturation magnetic moment, could be effectively changed by adding some foreign oxides [1,4,6,9,10]. However, the influence of such treatment on the thermal stability of lithium ferrites received less attention.

The present investigation reports a study on solid–solid interactions between Fe_2O_3 and Li_2CO_3, of varying compositions, and on the thermal stability of the lithium ferrites produced. The techniques employed were DTA, TG, DTG and X-ray diffraction.

EXPERIMENTAL

Materials

Two specimens of ferric oxide and lithium carbonate were prepared by mixing finely powdered well-crystallized α-Fe_2O_3 with Li_2CO_3 with the addition of a small amount of distilled water. The $Fe_2O_3 : Li_2CO_3$ molar ratios were 1 : 1 and 1 : 2. The solid samples produced were dried at 100 ° C and roasted 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 prepared Fe_2O_3–Li_2CO_3 solids were carried out using a Netzsch–Gerätebau simultaneous thermal analysis apparatus (STA 409, type 6.223). The rate of heating was kept at 10 ° C min^{-1}. A 50 mg sample of each solid specimen was employed in each case.

An X-ray investigation of the thermal products of various 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–Li_2CO_3 solids

Figures 1 and 2 represent DTA, TG and DTG curves of mixtures of ferric oxide and lithium carbonate having molar ratios of 1 : 1 and 1 : 2. Two

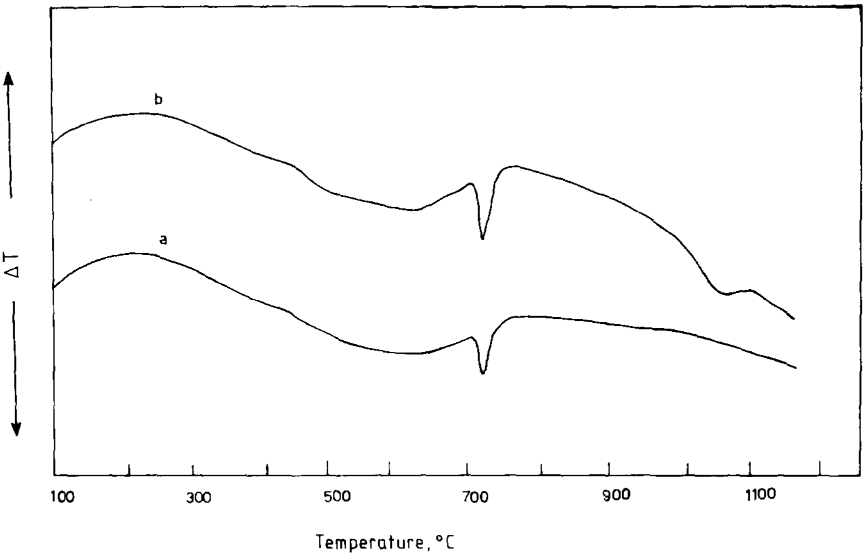

Fig. 1. DTA curves of mixtures of ferric oxide and lithium carbonate solids with the compositions (a) $Fe_2O_3:Li_2CO_3$ and (b) $Fe_2O_3:2Li_2CO_3$.

endothermic peaks are observed for the first solid; the first peak is broad extending between 400 and 650 ° C and the second peak is sharp and strong having its maximum located at 735 ° C. The solid having the composition $Fe_2O_3:2Li_2CO_3$ exhibits three endothermic peaks; the first peak is also broad extending between 400 and 650 ° C, the second peak is sharp and strong located at 735 ° C and the third peak is relatively sharp and strong located at 1080 ° C. The loss in weight accompanying the broad endothermic peak attains about 13% for both solids. The endothermic peak at 1080 ° C is followed by a 12% loss in weight. The loss in weight corresponding to the peaks at 735 ° C reaches 6% and 4% for the solids having the composition $Fe_2O_3:Li_2CO_3$ and $Fe_2O_3:2Li_2CO_3$ respectively. These two solids lose 24% and 32% of their weight when heated between room temperature and 1100 ° C.

The broad endothermic peak at 400–650 ° C might correspond to a solid–solid interaction between ferric oxide and lithium carbonate producing lithium ferric compound(s). In fact, it has been reported by Shorina and Lisnyak [6] that Fe_2O_3 interacted with Li_2CO_3 at temperatures starting from 450 ° C to yield lithium ferrite $LiFe_5O_8$. These researchers also showed that with increasing temperature and sintering time, the ferritization rate increased and the ferrite formation was completed at 800 ° C. The sharp endothermic peak at 735 ° C might indicate the decomposition of the unreacted portion of Li_2CO_3 into Li_2O [1,11] which interacted with Fe_2O_3 to form ferric lithium compound(s). The endothermic peak at 1080 ° C, only observed for the solid having the composition $Fe_2O_3:2Li_2CO_3$ might char-

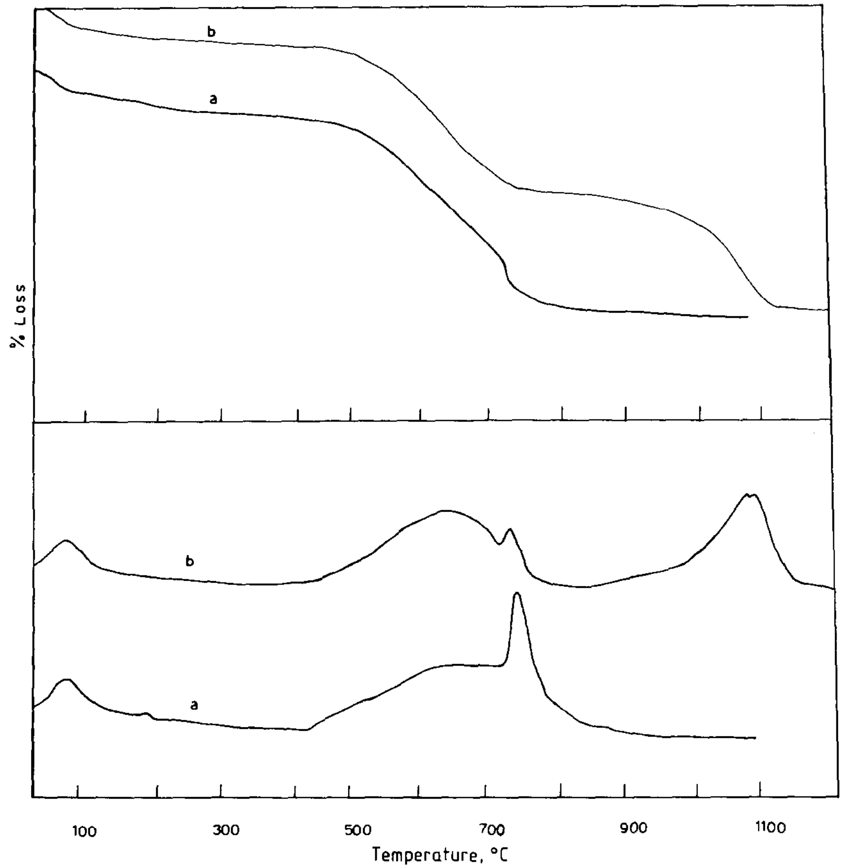

Fig. 2. TG and DTG curves of mixtures of ferric oxide and lithium carbonate solids with the compositions (a) $Fe_2O_3:Li_2CO_3$ and (b) $Fe_2O_3:2Li_2CO_3$.

acterize a decomposition process of lithium ferric compounds or more probably sublimation of Li_2O. The identification of lithium ferric compounds produced at different temperatures will be given using XRD measurements in the following section.

X-ray investigation of the thermal products of ferric oxide treated with different proportions of lithium carbonate

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 $Fe_2O_3:Li_2CO_3$ and $Fe_2O_3:2Li_2CO_3$ solids precalcined in air for 6 h at 500, 700, 800, 900, 1000 and 1100 °C. All the diffraction lines of the α-Fe_2O_3 and Li_2CO_3 phases, together with three lines of reasonable intensity, were detected in the diffraction patterns of the solids heated at

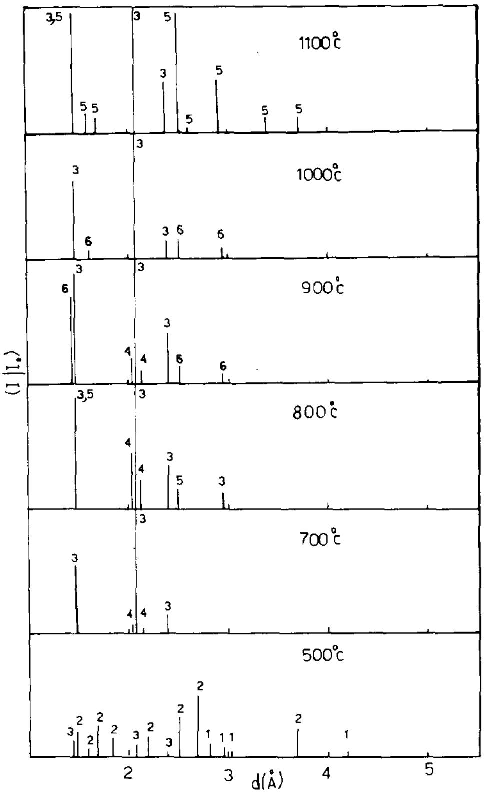

Fig. 3. X-ray diffraction patterns of the thermal products of the solid $Fe_2O_3:Li_2CO_3$ (1) Li_2CO_3, (2) α-Fe_2O_3, (3) α-$LiFeO_2$, (4) β-$LiFeO_2$, (5) α-$LiFe_5O_8$, (6) β-$LiFe_5O_8$.

500 ° C. The *d* spacings of these lines were calculated and found to be 2.08_x, $2.40_{0.8}$ and $1.47_{0.7}$.

These lines corresponded to the lithium ferrite phase, α-$LiFeO_2$ [12]. The formation of this compound might proceed according to the reaction

$$Fe_2O_3 + Li_2CO_3 \xrightarrow{500\text{-}700\,^\circ C} 2LiFeO_2 + CO_2(g)$$

The completion of this reaction should be followed by an 18.8% loss in weight of the reacting species. The observed loss in weight at temperatures between 450 and 650 ° C was only 13%, indicating the presence of unreacted portions of both ferric oxide and lithium carbonate.

It can be shown from Figs. 3 and 4 that the increase in the precalcination temperature up to 700 ° C resulted in the disappearance of the characteristic diffraction lines of α-Fe_2O_3 and in a considerable decrease in the intensity of the lines corresponding to the free Li_2CO_3 phase with a subsequent increase in the intensity of the diffraction lines of the α-$LiFeO_2$ phase. These results clearly indicate that ferric oxide interacted almost completely with Li_2CO_3 at 700 ° C, yielding α-$LiFeO_2$.

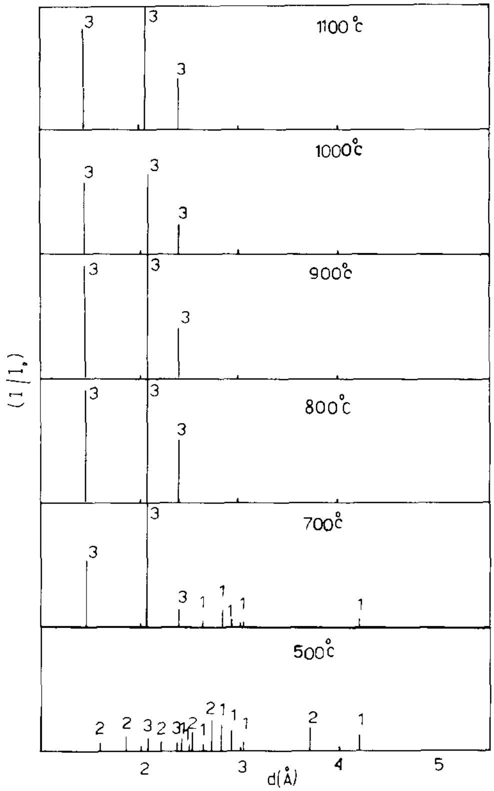

Fig. 4. X-ray diffraction patterns of the thermal products of the solid $Fe_2O_3:2Li_2CO_3$ (1) Li_2CO_3, (2) α-Fe_2O_3, (3) α-$LiFeO_2$.

The rise in roasting temperature to 800 °C led to the disappearance of the diffraction lines of free lithium carbonate, indicating its decomposition into Li_2O which interacted readily with Fe_2O_3, present in minute amounts and therefore not detected by XRD, producing α lithium ferrite. The lithium oxide formed might also dissolve in the $LiFeO_2$ lattice [1,10]. The formation of lithium ferrite at 800 °C might occur according to the reaction

$$Fe_2O_3 + Li_2O \xrightarrow{800\,^\circ C} 2LiFeO_2(\alpha)$$

When the precalcination temperature of the $Fe_2O_3 : Li_2CO_3$ solid reached 900 °C, the α-$LiFeO_2$ produced underwent partial phase transformation into β-$LiFeO_2$ and α-$LiFe_5O_8$. The intensity of the diffraction lines of the first phase is bigger than that of the lines corresponding to the second phase. This might indicate that the amount of α-$LiFe_5O_8$ is much smaller than the amount of β-$LiFeO_2$. The formation of lithium ferrite in the form of α-$LiFe_5O_8$ might take place according to the reaction

$$2Fe_2O_3(\alpha) + LiFeO_2(\alpha) \xrightarrow{900\,^\circ C} LiFe_5O_8(\alpha)$$

The diffraction lines of both β-$LiFeO_2$ and α-$LiFe_5O_8$ disappeared from the patterns of the $Fe_2O_3:Li_2CO_3$ solid preheated at 1000 °C (Fig. 3). The patterns of this solid include the diffraction lines of α-$LiFeO_2$, with the highest intensity, together with three other lines. The *d* spacings of these lines were calculated and found to be 2.53_x, $2.97_{0.5}$ and $1.61_{0.4}$. These lines correspond to β-$LiFe_5O_8$ [12]. The formation of this compound might occur according to the reaction

$$2Fe_2O_3 + LiFeO_2(\alpha \text{ and } \beta) \xrightarrow{1000\,°C} LiFe_5O_8(\beta)$$

The augmentation of the calcination temperature of the $Fe_2O_3:Li_2CO_3$ solid to 1100 °C resulted in a complete disappearance of the lines of the β-$LiFe_5O_8$ phase with the subsequent appearance of all the diffraction lines of α-$LiFe_5O_8$ together with the lines of the α-$LiFeO_2$ phase. The intensities of the main lines of the two α ferrite phases are almost the same which might indicate their presence in equivalent amounts. The absence of any exothermic or endothermic peaks in the DTA curve of the solid having the composition $Fe_2O_3:Li_2CO_3$ at temperatures between 1000 and 1100 °C, might show that the phase transformation β-$LiFe_5O_8 \rightarrow \alpha$-$LiFe_5O_8$ occurred at a relatively slow rate and/or its occurrence is not accompanied by an important thermal effect.

Concerning the solids having the composition $Fe_2O_3:2Li_2CO_3$, the diffraction lines of the well-crystallized α-$LiFeO_2$ phase were only detected in the patterns of the specimens precalcined in air at temperatures between 800 and 1100 °C (Fig. 4). These results clearly indicate that the presence of an excess of lithium, more than is required for the formation of lithium ferrites, resulted in an important increase in the thermal stability of the α-$LiFeO_2$ phase and prevented its transformation to any other ferrite phase. The absence of free lithium oxide in these solids indicated that it had dissolved in the lattice of the $LiFeO_2$ solid produced. It has been shown in ref. 13 that lithium oxide dissolved in a Co_3O_4 solid with a spinel structure [14] much increased its thermal stability and prevented its decomposition into CoO even when heated at 1100 °C. Pure Co_3O_4 is known to decompose on heating in air at about 850 °C yielding CoO [13]. It is plausible that lithium ions could be dissolved in the lattice of α-$LiFeO_2$ by substituting some of the host iron cations and/or through location in interstitial positions of the host lattice. The solid solution produced has remarkable thermal stability. The dissolution of Li_2O in $LiFeO_2$ might create some lattice defects in the ferrite lattice such as the transformation of some iron cations to a high valence state and/or the creation of anionic vacancies [15,16]. The identification of such lattice defects lies beyond the scope of this work. The X-ray characteristics of the Li_2O–$LiFeO_2$ solid solution might be different from those of pure lithium ferrite. However, the *d* spacings of both compounds are almost the same, indicating the absence of an effective broadening due to dissolution of Li_2O in the $LiFeO_2$ lattice. Nevertheless, the relative intensity of the diffraction line at $d = 2.40$ Å, one of the main lines of the α-$LiFeO_2$ phase, was found to decrease from 50% to 40% and 20% and then increased to 40% for $Fe_2O_3 : 2Li_2CO_3$ solids calcined at 800, 900, 1000 and 1100 °C respectively. Furthermore, the intensity of all the diffraction lines of α-$LiFeO_2$ suffered a decrease of about 35% by increasing the calcination temperature from 900 to 1000 °C. These results might indicate some type of disordering of the α-$LiFeO_2$ lattice due to dissolution of Li_2O. This effect attains a maximum at a calcination temperature of 1000 °C.

The endothermic peak observed at 1080 °C in the DTA curve of $Fe_2O_3 : 2Li_2CO_3$, accompanied by a 12% loss in weight (Fig. 1), might correspond to the departure of some Li_2O from the $LiFeO_2$ by sublimation from the outermost surface layers of the ferrite phase. The complete sublimation of Li_2O from the $LiFeO_2$ lattice should be accompanied by a 25% loss in weight. However, the amount of Li_2O remaining in the solid preheated at 1100 °C was sufficient to stabilize the α-$LiFeO_2$ phase.

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