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Thermochimica Acta 272 (1996) 11–26

thermochimica
acta

The thermal decomposition of coprecipitates and physical mixtures of magnesium-iron oxalates[1]

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Received 11 May 1995; accepted 4 June 1995

Abstract

Physical mixtures and coprecipitates of magnesium and divalent iron oxalates having molar ratios of 1:1, 1:2 and 1:4 were prepared. Comparisons were made between the thermal decomposition of the physically mixed oxalate and the coprecipitated oxalate having the same composition. Samples were studied by thermogravimetry (TG), thermomagnetometry (TM), differential thermal analysis (DTA), mass spectroscopic evolved gas analysis (EGA), and powder X-ray diffraction from 25 to 1400°C in both oxidizing and inert atmospheres. Coprecipitates were expected to be solid solutions, showing only single weight losses for the dehydration and decomposition steps. This is true for the coprecipitates having more iron present than magnesium. In contrast, the physical mixtures were expected to behave as separate materials, showing two separate weight losses for dehydration and decomposition. This held true except for the dehydration step, which takes place as one weight loss. TM and X-ray diffraction results indicate the coprecipitate forms magnesium ferrite ($MgFe_2O_4$) more readily than the equivalent physically mixed material. An oxidizing atmosphere was necessary to facilitate the production of magnesium ferrite.

Keywords: Magnesium-iron oxalates; Decomposition

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1. Introduction

Ferrites find extensive use as electronic materials due to their magnetic properties, combined high resistivity, and consequently low eddy current and low dielectric loss.

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[1] Presented at the 23rd North American Thermal Analysis Society Conference, Toronto, Ont., Canada, 25–28 September, 1994.

SSDI 0040-6031 (95) 02626-6

These properties depend upon the precise stoichiometry, oxygen defects, and microstructure of the final product. This study compared the decomposition of coprecipitated oxalates and physically mixed oxalates having the same composition.

The coprecipitates were to be made using the method of coprecipitation known as the "clean oxalate method" [1,2]. This method reacts hydroxides or carbonates with oxalic acid to form the final coprecipitate product. The hydroxides and carbonates form only water and carbon dioxide as the byproducts. It could not be used for this study to prepare the coprecipitates, due to the instability of iron(II) carbonate and hydroxide. Therefore, soluble salts of sulfates were used in the preparation.

The decomposition of oxalates do not all follow the same scheme. Three different mechanisms have been determined depending upon the stability of the cation's oxidation state and its carbonate [3]. The first mechanism is for those cations that are easily reduced, like Ni(II), to form the metal as the final product in an inert atmosphere. A second mechanism is for those cations, like calcium, that form a stable carbonate on decomposition in an inert atmosphere. The third mechanism is for those cations, like Fe(II), which form metal oxides as the final products. In an oxidizing atmosphere all the above ultimately form metal oxides.

Magnesium and iron(II) oxalate should behave according to the third mechanism described above. Also, TG for the physical mixtures should show that the physical mixtures behave as two separate materials. The decomposition of the coprecipitates should act as a solid solution, behaving as a single compound [4,5]. The TG should show two weight losses: the first for the dehydration reaction and the second for the decomposition of the anhydrous oxalate.

Fig. 1 shows the phase diagram for magnesium oxide and iron(III) oxide in air [6]. This phase diagram will be used to help explain the end products. The 1:1 Mg/Fe sample should give final products of magnesium oxide and magnesium ferrite, the 1:2 Mg/Fe sample magnesium ferrite, and the 1:4 Mg/Fe sample products of magnesium ferrite and iron(III) oxide. X-Ray diffraction will aid in the determination of the final products, but if the products have the same crystal structure, it will not help. TM is very useful in dis-

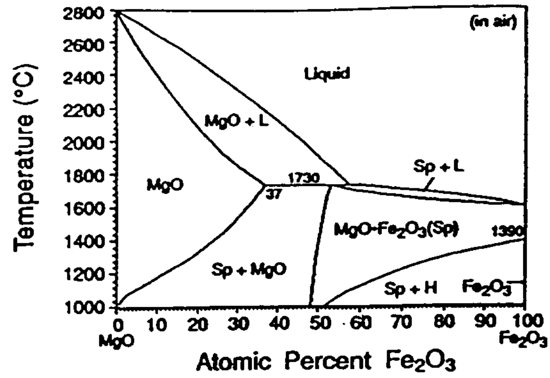

Fig. 1. Phase diagram of MgO–Fe$_2$O$_3$ system in air [6].

tinguishing between these products if they have magnetic properties, because each product should have a unique Curie temperature, T_c.

2. Experimental and results

2.1. Synthesis

The physically mixed and coprecipitated oxalates were both prepared in the laboratory. The clean oxalate method was used to prepare the individual oxalates needed for the physical mixtures, but was not used for the preparation of the coprecipitates due to the instability of iron(II) carbonate in air. The physical mixtures were prepared by mixing magnesium and iron(II) oxalates to give the desired molar ratios of magnesium to iron. The coprecipitates were prepared by precipitating from solution an oxalate compound containing the desired magnesium to iron molar ratio.

Magnesium oxalate was prepared by reacting magnesium carbonate with a 5% excess of 1.034 molar oxalic acid. The mixture was stirred for several hours. The white precipitate was filtered, washed with water, and given a final rinse with acetone.

Iron(II) oxalate was prepared in a dry bag flushed with high purity grade nitrogen gas. Iron(II) sulfate and ammonium carbonate, both of which were assayed by TG for their water content, were used to prepare iron(II) carbonate. The iron(II) carbonate was then reacted with a 5% excess of 1.003 molar oxalic acid solution and allowed to stir for several hours. The yellow precipitate was filtered, washed with water, and rinsed with acetone.

Physical mixtures were prepared by mixing appropriate amounts of the individual oxalates to give the appropriate magnesium to iron(II) molar ratios. The desired mixtures were shaken for several minutes, ground in an agate mortar and pestle, and reshaken.

Table 1

Sample mass used for TG analysis of the individual physical mixtures at 5°C min^{-1} and 20°C min^{-1}, in flowing air or argon

Ratio Mg/Fe	Sample mass/mg	Heating rate/(°C min^{-1})	Dynamic atmosphere
1:1	5.728	20	Air
	6.819	20	Argon
	7.751	5	Air
	6.605	5	Argon
1:2	7.323	20	Air
	8.137	20	Argon
	7.742	5	Air
	6.818	5	Argon
1:4	8.794	20	Air
	6.603	20	Argon
	7.234	5	Air
	8.459	5	Argon

Table 2

Sample mass used for TG analysis of the coprecipitates at 5°C min^{-1} and 20°C min^{-1}, in flowing air or argon

Ratio Mg/Fe	Sample mass/mg	Heating rate/(°C min^{-1})	Dynamic atmosphere
1:1	8.972	20	Air
	8.377	20	Argon
	8.160	5	Air
	8.725	5	Argon
1:2	8.411	20	Air
	7.974	20	Argon
	8.573	5	Air
	8.380	5	Argon
1 :4	8.940	20	Air
	8.476	20	Argon
	9.227	5	Air
	8.345	5	Argon

Coprecipitates were prepared by mixing magnesium and iron(II) sulfates having the appropriate molar ratios in distilled water with magnetic stirring. Once dissolved the mixture was added, via a 50 ml buret, to a 5% excess of ammonium oxalate solution over

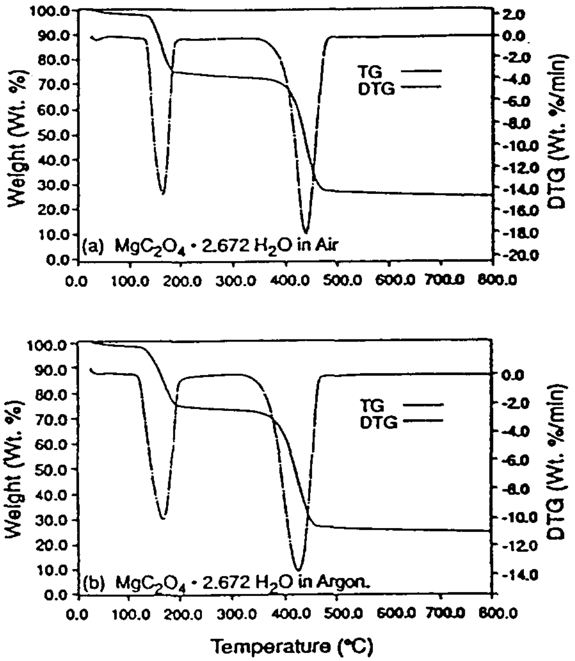

Fig. 2. TG and DTG curves of $MgC_2O_4 \cdot 2.672H_2O$ at a heating rate of 20°C min^{-1} in flowing air or argon. (a) 5.622 mg in flowing air; (b) 12.138 mg in flowing argon.

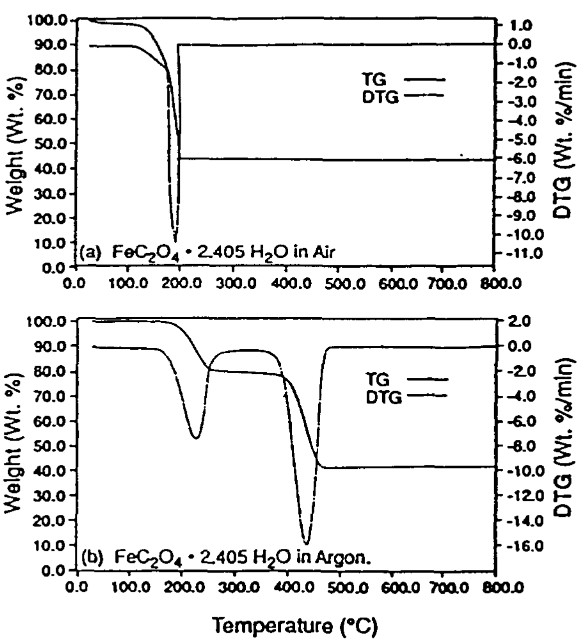

Fig. 3. TG and DTG curves of $FeC_2O_4 \cdot 2.405H_2O$ at a heating rate of 20°C min^{-1} in flowing air or argon. (a) 9.657 mg in flowing air; (b) 7.527 mg in flowing argon.

ice with stirring. The yellow precipitates were then filtered, washed with water, and rinsed with acetone.

2.2. Thermogravimetry (TG)

TG was performed on the individual, physically mixed, and coprecipitated oxalates using a Perkin-Elmer TGA7 Thermogravimetric Analyzer. The samples were studied at heating rates of 5 and 20°C min^{-1} in flowing air or argon at rates of approximately 50 ml min^{-1}. The sample sizes are given in Tables 1 and 2.

TG and DTG curves for the pure oxalates at a heating rate of 20°C min^{-1} in flowing air are shown in Figs. 2 and 3. The dehydration reaction for both oxalates in air and argon takes place between 125 and 200°C. The decomposition of the anhydrous magnesium oxalate takes place between 390 and 500°C in both flowing air and argon. The decomposition of the anhydrous iron(II) oxalate is very different in an oxidizing atmosphere than in an inert atmosphere. In air the decomposition occurs almost immediately after dehydration. The loss occurs so quickly because of the violent exothermic oxidation of the carbon monoxide and iron(II). The strong exotherm dominates the decomposition in air and a thermal runaway occurs. In argon the oxidation is not as violent, thus shifting the decomposition to between 300 and 350°C.

The decomposition of the individual oxalates is important for two reasons. The first is to determine the amount of water in the materials used to prepare the physical mixtures.

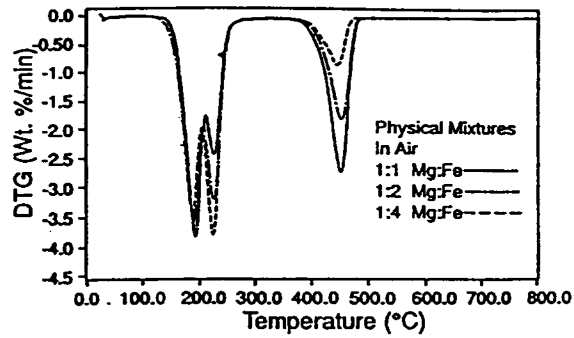

Fig. 4. DTG curves of the individual physically mixed oxalates at 5°C min^{-1} in flowing air. ——, 1:1 Mg/Fe, 7.751 mg; – – – -, 1:2 Mg/Fe, 7.742 mg; - - - - -, 1:4 Mg/Fe, 7.234 mg.

The second reason is to get an indication of what the composite decomposition curve of the physically mixed oxalates should look like. This aids in the interpretation and direct comparison of the physical mixtures to the coprecipitates.

The DTG curves for the physical mixtures in air and argon at a heating rate of 5°C min^{-1} are shown in Figs. 4 and 5. The first weight loss, the dehydration reaction representative of the combined oxalates, occurs between 125 and 225°C in air and argon. The second weight loss in air occurs between 225 and 270°C, while in argon the loss occurs between 350 and 400°C. The second weight loss is identified as the decomposition of the anhydrous iron(II) oxalate. The evidence to prove this is twofold. The first is the temperature region where weight loss occurs is similar to that for the pure iron(II) oxalate. The second reason is that the area under the derivative (DTG) curves for that peak increases as the proportion of iron(II) oxalate increases in the sample.

The third weight loss occurs between 450 and 530°C in air and argon at heating rates of 5 or 20°C min^{-1}. The weight loss corresponds to the decomposition of the anhydrous magnesium oxalate. This is evident by following the area under the DTG curves as the

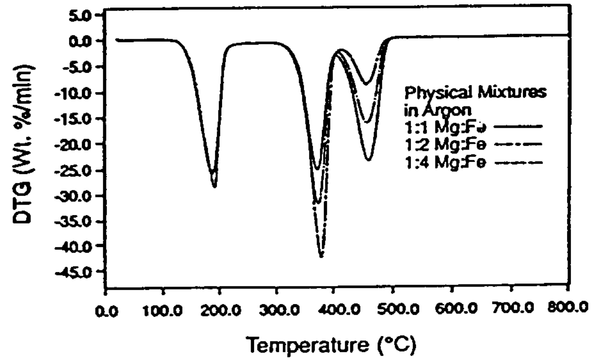

Fig. 5. DTG curves of the individual physically mixed oxalates at 5°C min^{-1} in flowing argon. ——, 1:1 Mg/Fe, 6.605 mg; – — -, 1:2 Mg/Fe, 6.818 mg; - - - - -, 1:4 Mg/Fe, 8.459 mg.

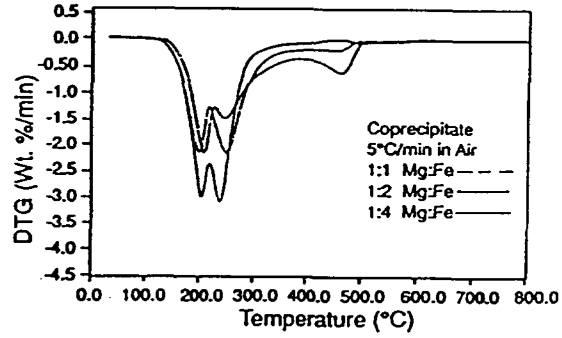

Fig. 6. DTG curves of the individual coprecipitated oxalates heated at 5°C min^{-1} in flowing air. - - - - -, 1:1 Mg/Fe, 8.130 mg; – – – -, 1:2 Mg/Fe, 8.573 mg; ——, 1:4 Mg/Fe, 9.227 mg.

ratio of the magnesium to iron(II) changes. Also comparison with the pure magnesium oxalate will indicate that the weight loss occurs in the same temperature range.

The DTG curves of the coprecipitates at a heating rate of 5°C $^{-1}$min in air and argon are shown in Figs. 6 and 7. The dehydration occurs between 125 and 230°C in air. In argon, the dehydration takes place in two steps. The first step is a major weight loss between 125 and 230°C. The second step is a slight weight loss occurring between 220 and 290°C. The second step becomes smaller as the amount of magnesium decreases. This peak could be due to initial supersaturation of the solution with magnesium oxalate during the synthesis because insufficient iron for complete nucleation and coprecipitation of the magnesium-iron(II) oxalates, followed by a post-precipitation of essentially pure magnesium oxalate.

Decomposition of the anhydrous oxalate occurs between 225 and 300°C in air or 320 and 420°C in argon. The final weight loss occurs between 420 and 500°C in air or 420 and 540°C in argon. The final weight loss is most evident for the 1:1 Mg/Fe sample. It is assumed that this weight loss is due to the small amount of separate magnesium oxalate

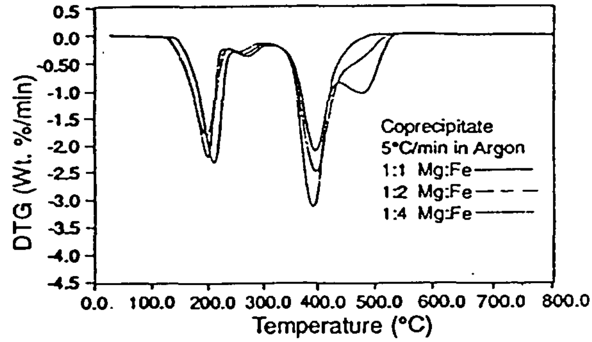

Fig. 7. DTG curves of the individual coprecipitated oxalates at 5°C min^{-1} in flowing argon. ——, 1:1 Mg/Fe, 8.725 mg; - - - - -, 1:2 Mg/Fe, 8.380 mg; – – – -, 1:4 Mg/Fe, 8.345 mg.

that was formed during the coprecipitation process. Note that the weight loss decreases as the amount of magnesium decreases and is barely detected for the 1:4 Mg/Fe sample.

2.3. Thermomagnetometry (TM)

A Perkin-Elmer TGA7 Thermogravimetric Analyzer equipped with a small permanent magnet was used for the TM measurements. The magnet was kept in the same position as much as possible, so that the magnetic field gradient affecting the samples was the same. An alumina pan was used instead of the typical platinum pan, because iron tends to alloy with the platinum causing a magnetic change that is not reflective of the sample of interest. The pure iron(II) oxalate, physical mixtures, and coprecipitates were analyzed in air and argon. The temperature range was from 30 to 975°C at rates of 5 and 20°C min^{-1}. The samples were then allowed to cool. The samples were heated and cooled once again at the same rates. Data were collected during both heating and cooling of the samples.

TM was performed on the samples to determine what magnetic phases were present in the material. Such data are very helpful in determining phases that have nearly the same X-ray diffraction pattern. This problem occurs with magnetite and magnesium ferrite. Fortunately they have very different values of T_c. The reported values for α-Fe_2O_3 are between 675 and 710°C [7,8]. The reported value for Fe_3O_4 is 585°C [8] and for $MgFe_2O_4$ is between 400 and 440°C [8].

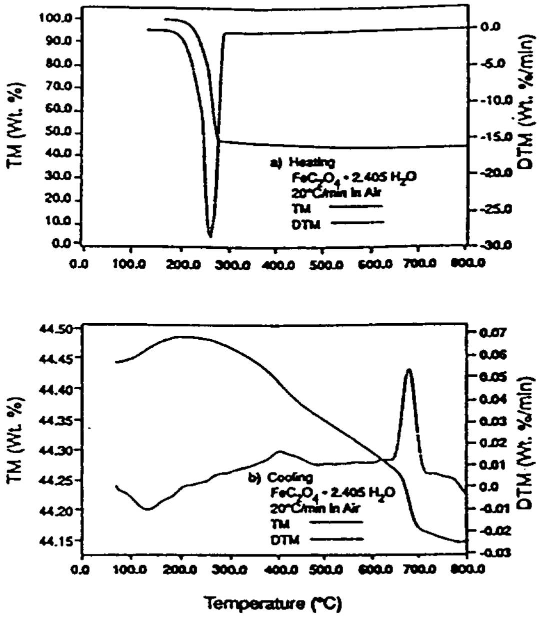

Fig. 8. TM and DTM heating and cooling curves, at a rate of 20°C min^{-1}, for $FeC_2O_4 \cdot 2.405H_2O$, 7.490 mg, in flowing air. (a) Heating; (b) cooling.

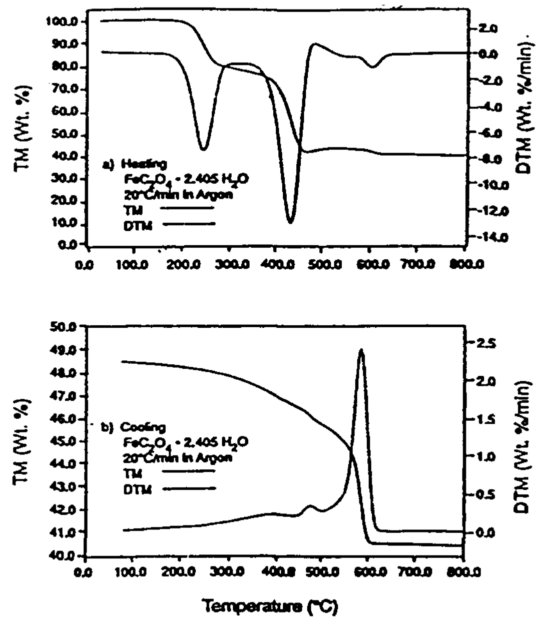

Fig. 9. TM and DTM heating and cooling curves, at a rate of 20°C min^{-1}, for $FeC_2O_4 \cdot 2.405H_2O$, 8.051 mg, in flowing argon. (a) Heating; (b) cooling.

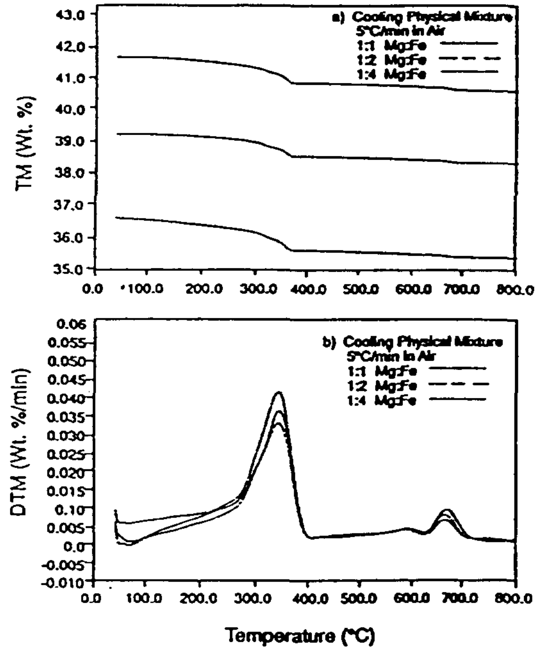

Fig. 10. TM and DTM cooling curves of the physical mixtures at 5°C min^{-1} in flowing air. (a) TM cooling curves: ——, 1:1 Mg/Fe, 8.253 mg; - - - - -, 1:2 Mg/Fe, 8.306 mg; — — — -, 1:4 Mg/Fe, 8.079 mg; (b) DTM cooling curves; — — — -, 1:1 Mg/Fe; - - - - , 1:2 Mg/Fe; ——, 1:4 Mg/Fe.

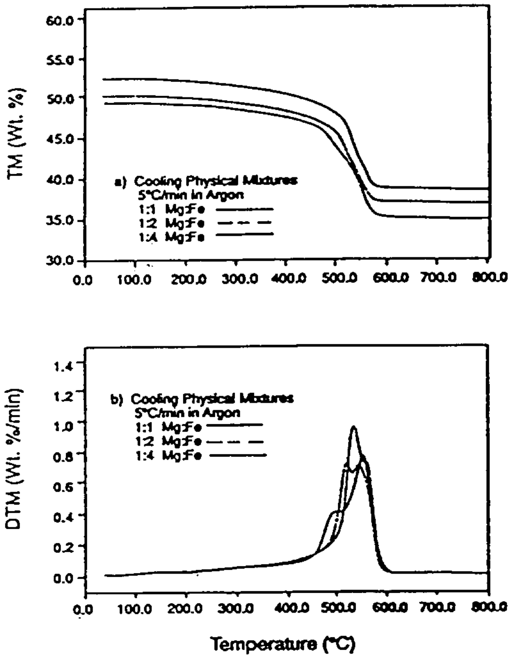

Fig. 11. TM and DTM cooling curves of the physical mixtures at 5°C $\min^{-1}$ in flowing argon. (a) TM cooling curves; - - - -, 1:1 Mg/Fe, 7.373 mg; - - - - -, 1:2 Mg/Fe, 7.988 mg; ——, 1:4 Mg/Fe, 8.219 mg; (b) DTM cooling curves; ——, 1:1 Mg/Fe; - - - - -, 1:2 Mg/Fe; - - - -, 1:4 Mg/Fe.

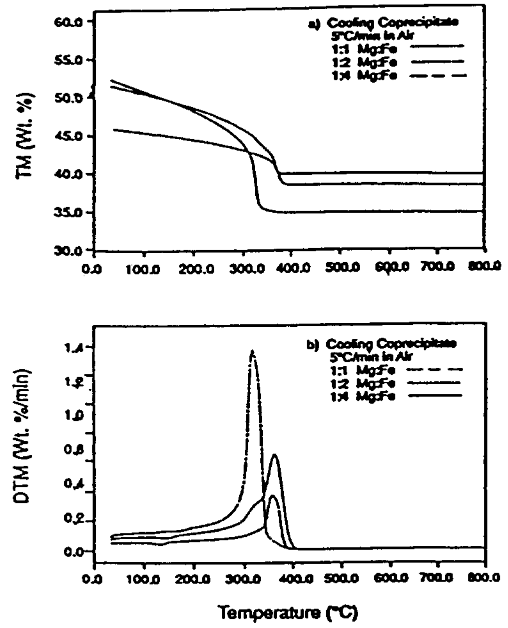

Fig. 12. TM and DTM cooling curves of the coprecipitates at 5°C $\min^{-1}$ in flowing air. (a) TM cooling curves; ——, 1:1 Mg/Fe, 7.953 mg; - - - -, 1:2 Mg/Fe, 8.107 mg; - - - - -, 1:4 Mg/Fe, 8.450 mg; (b) DTM cooling curves; - - - - -, 1:1 Mg/Fe; ——, 1:2 Mg/Fe; - - - -, 1:4 Mg/Fe.

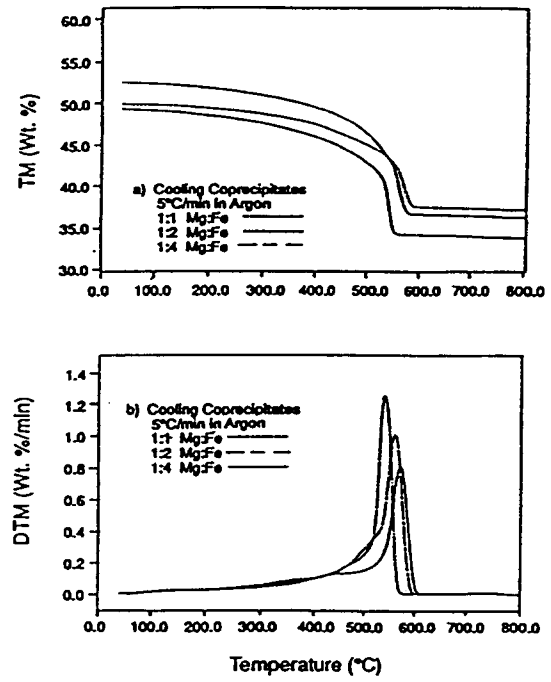

Fig. 13. TM and DTM cooling curves of the coprecipitates at 5°C min^{-1} in flowing argon. (a) TM cooling curves; ——, 1:1 Mg/Fe, 8.530 mg; - - - -, 1:2 Mg/Fe, 8.368 mg; - - - - -, 1:4 Mg/Fe, 8.498 mg; (b) DTM cooling curves; - - - -, 1:1 Mg/Fe; - - - - -, 1:2 Mg/Fe; ——, 1:4 Mg/Fe.

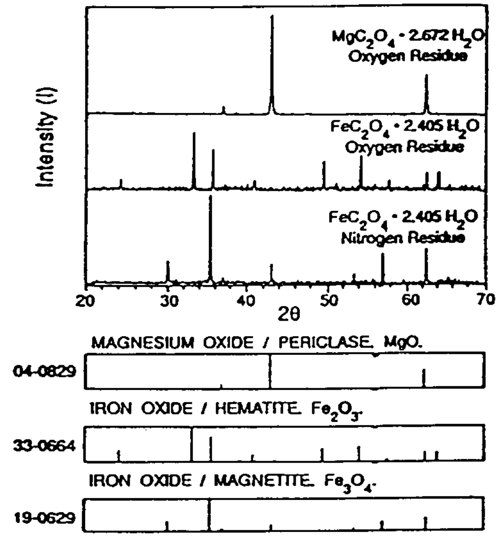

Fig. 14. X-Ray diffraction patterns of the magnesium oxalate oxygen residue, the iron(II) oxygen residue, and the iron(II) nitrogen residue. Samples were prepared externally in a Lindburg furnace heated to a temperature of 1000°C. Experimental conditions of the XRD: CuKα radiation; working voltage, 45 kV; working current, 20 mA; 20° < 2θ < 70°; scanned at 1° min^{-1}.

TM and DTM results in air for pure iron(II) oxalate are shown in Fig. 8. Fig. 8b shows the TM and DTM of the sample upon cooing. The T_c occurs around 685°C, which is near the reported value for α-Fe_2O_3. The apparent mass change is very small so the scale is expanded.

TM and DTM results in argon are shown in Fig. 9. The T_c occurs around 585°C, which agrees with the literature value for magnetite. The T_c in argon is seen both on heating and cooling. The initial cooling curve shows signs of a small amount of a second phase, however, a second heating and cooling of the sample showed this phase to disappear.

The cooling curves for the TM and DTM of the physical mixtures heated at 5°C min^{-1} in air are shown in Fig. 10, while the curves for argon are shown in Fig. 11. In air, the product was multiphase with an apparent weight gain occurring for α-Fe_2O_3 around 675°C and another around 385°C. This suggests magnesium ferrite formation is incomplete. In argon, there is a magnetic transition taking place around 585°C for all three samples, this transition indicates the presence of magnetite. A second transition occurs between 510 and 560°C. The T_c increases as the amount of iron in the sample increases. This shows that the non-magnetic magnesium is a substitutional impurity and lowers the magnetic transition temperature of the spinel formed.

The TM and DTM curves for the coprecipitates in air are shown in Fig. 12, while the curves for argon are shown in Fig. 13. In air, the coprecipitates show a magnetic transition taking place between 340 and 400°C. The 1:1 Mg/Fe sample shows only a single transition around 340°C. This transition is due to the formation of magnesium ferrite with the substitution of some magnesium oxide lowering the T_c. The other 1:2 Mg/Fe sample shows a multiple phase in this region. Upon further heating and cooling the sample becomes single phase. The 1:4 Mg/Fe also shows a T_c around 670°C for α-Fe_2O_3. In argon, a single magnetic phase having a T_c between 560 and 590°C occurs. The 1:1 sample shows a lower T_c due to the excess magnesium oxide incorporated into the system.

2.4. X-Ray diffraction

X-Ray diffraction patterns of the powders were collected using an automated Scintag PADV X-ray diffractometer with Cu$K\alpha$ radiation and a gas proportional counter as the detector. Operating conditions for the diffractometer were a voltage of 45 kV and current of 20 mA. A continuous scan of 1° min^{-1} with step size of 0.03° was used to obtain the powder patterns over a 2θ range of 10–70°. The data were collected and processed using the DMS version 2.0 Scintag software. Powder patterns were collected on the uncalcined samples, oxidized residues, and residues from samples fired in an inert atmosphere. Calcination was performed externally and the atmosphere controlled.

X-Ray patterns were collected for the oxidized and inert residues to aid in interpretation of the TG and TM data. The powder patterns collected for the pure oxalates are shown in Fig. 14. The magnesium oxalate powder pattern in both an oxidizing and inert atmosphere was magnesium oxide (periclase). The iron(II) oxalate residue in an oxidizing atmosphere was α-Fe_2O_3 (hematite). The pattern of the iron(II) oxalate residue in an inert atmosphere was Fe_3O_4 (magnetite).

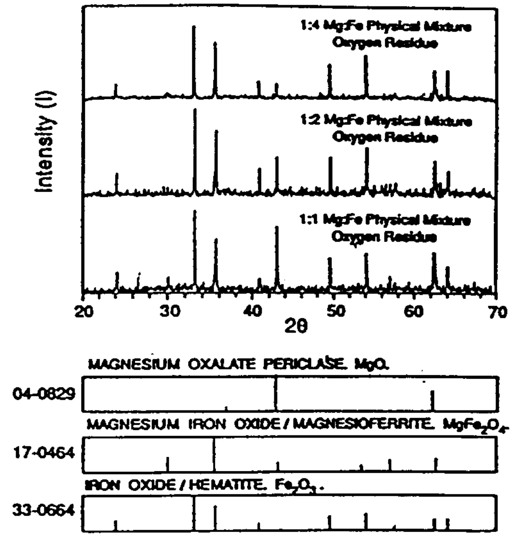

Fig. 15. X-Ray diffraction patterns of the oxygen residues of the individual physically mixed oxalates. Samples were prepared externally in a Lindburg furnace heated to a temperature of 1000°C. Experimental conditions of the XRD: CuKα radiation; working voltage, 45 kV; working current, 20 mA; $20° < 2\theta < 70°$; scanned at 1° min^{-1}.

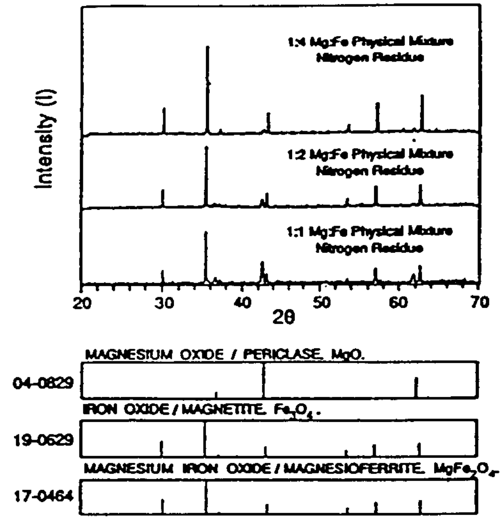

Fig. 16. X-Ray diffraction patterns of the nitrogen residues of the individual physically mixed oxalates. Samples were prepared externally in a Lindburg furnace heated to a temperature of 1000°C. Experimental conditions of the XRD: CuKα radiation; working voltage, 45 kV; working current, 20 mA; $20° < 2\theta < 70°$; scanned at 1° min^{-1}.

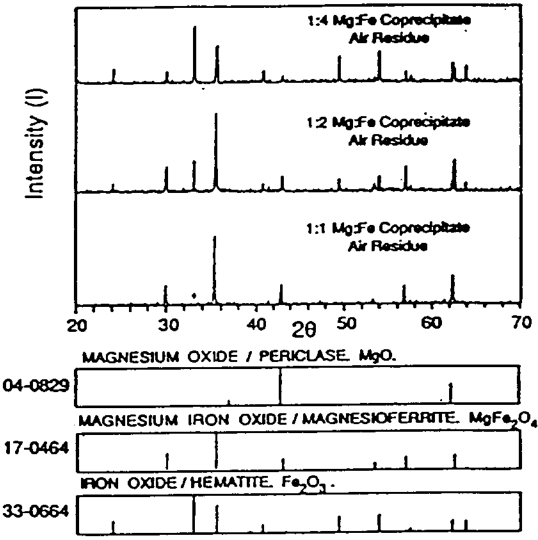

Fig. 17. X-Ray diffraction patterns of the air residues of the individual coprecipitated oxalates. Samples were prepared externally in a Lindburg furnace heated to a temperature of 1000°C. Experimental conditions of the MD: CuKα radiation; working voltage, 45 kV; working current, 20 mA; $20° < 2\theta < 70°$; scanned at 1° min^{-1}.

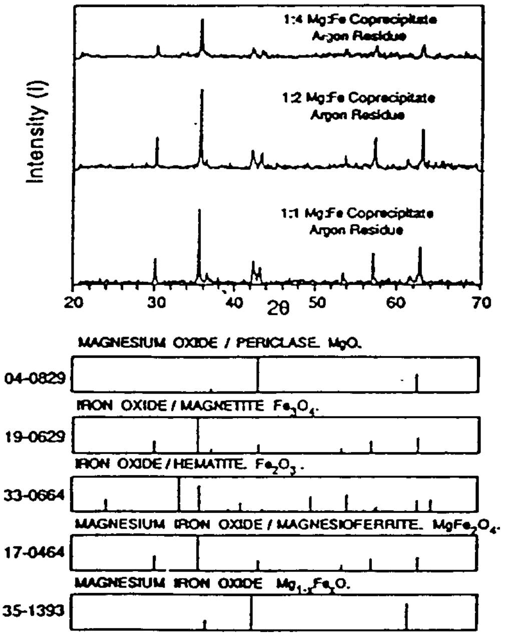

Fig. 18. X-Ray diffraction patterns for the argon residues of the individual coprecipitated oxalates. Samples were prepared externally in a Lindburg furnace heated to a temperature of 1000°C. Experimental conditions of the XRD: CuKα radiation; working voltage, 45 kV; working current, 20 mA; $20° < 2\theta < 70°$; scanned at 1° min^{-1}.

Powder patterns for the oxidized residues of the physical mixtures are shown in Fig. 15. They match those of hematite and magnesium oxide. A slight indication of the magnesium ferrite is present as seen by the peak at a 2θ of 30° and a side shoulder at 2θ of 35°. Those peaks are most evident in the 1:1 Mg/Fe sample. The powder patterns for the inert residues, in Fig. 16, show mainly a spinel structure and magnesium oxide. TM confirmed the spinel structure to be magnetite with a T_c of 585°C.

The powder patterns for the oxidized residue for the coprecipitates are shown in Fig. 17. The 1:1 Mg/Fe sample is magnesium ferrite and magnesium oxide. The 1:2 and 1:4 Mg/Fe samples are magnesium ferrite and hematite, proven by TM. The inert residues, in Fig. 18, are shown to have powder patterns resembling a spinel structure and magnesium oxide. The TM data shows the spinel structure to be that of magnetite.

3. Summary

The goals of the study were to show that the coprecipitated oxalates would behave as a single compound, that the coprecipitates would form the final products more readily than the physical mixtures, and finally to demonstrate the usefulness of TM in studying materials that have magnetic properties.

The coprecipitated mixtures were expected to behave as single material, showing only single symmetrical weight losses for dehydration and decomposition. In contrast, the physical mixtures were expected to have poorly resolved weight losses for dehydration and well resolved individual weight losses for the anhydrous oxalate decomposition.

The combination of all the techniques showed the physical mixtures to decompose in three steps as expected. The coprecipitates, although expected to decompose in two steps, showed a third step around 400°C. This step resembled the final mass loss for the individual magnesium oxalate. This weight loss diminished as the amount of magnesium in the sample decreased. The weight loss was barely detected for the 1:4 Mg/Fe sample.

The use of TM was helpful in determining what magnetic phases were formed during decomposition of the samples and interpreting the results determined by X-ray diffraction. The TM in combination with the X-ray diffraction showed that an oxidizing atmosphere was necessary for the production of magnesium ferrite. The physical mixtures show magnesium ferrite and hematite to be products for all three samples. The coprecipitates show magnesium ferrite as the product for all three samples and hematite for the 1:4 Mg/Fe sample. The intensity of the magnesium ferrite magnetic transition for the coprecipitates is seen to be much stronger than for the physical mixtures. These data in combination with the X-ray diffraction patterns for the oxidized residues indicates that the coprecipitate forms the magnesium ferrite more readily than the corresponding physical mixture.

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