Thermochimica Acta, 14 (1976) 159–167
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SIMULTANEOUS HOT PRESSING AND DIFFERENTIAL THERMAL ANALYSIS

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ABSTRACT

Differential thermal analysis was used to investigate the formation of lead hexaferrite from coprecipitated basic lead carbonate and hydrated ferric oxide at pressures up to 15 000 psi and temperatures up to 885°C.

To overcome pressure sensitivity problems, a system was designed to maintain both junctions of the differential thermocouple at the experimental pressure. One junction was situated in the reacting mixture in the hot pressing mold cavity, the other in a standard material in between the two halves of a split bottom plunger. Mold temperatures were separately measured at atmospheric pressure. Heating rates of about 8°C min^{-1} were used.

Differential traces at various pressures showed a monotonously similar lack of clearly defined features. However, two features became obvious on each after subtracting a "composite baseline" consisting of a normal baseline and differential traces for basic lead carbonate and hydrated ferric oxide in the appropriate proportions.

Corrected traces showed a pressure-insensitive exothermic peak at 475°C, tentatively ascribed to grain growth caused by the mineralising action of trapped water vapour. A pressure-sensitive exothermic peak at temperatures from 675 to 635°C over the applied pressure range 0 to 15 000 psi was related to lead oxide–iron oxide compound formation. This correlates well with published phase equilibrium diagram information.

INTRODUCTION

There are two classes of magnetic oxide ceramics. One class is called "soft" and is typified by the naturally occurring mineral magnetite [Fe_3O_4]. The other class is called "hard" and is typified by lead hexaferrite which has the magnetoplumbite structure[1], magnetoplumbite being a naturally occurring mineral[2] $[Pb[Fe_{7.5}Mn_{3.5}Al_{0.5}Ti_{0.5}]O_{19}]^3$.

The essential difference between soft and hard ferrites is their behaviour in an oscillating magnetic field. Soft ferrites show large remnant magnetisation but small

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*Presented at the 5th North American Thermal Analysis Society Meeting, Peterborough, Ontario, Canada, June 8–14, 1975.

coercive force, i.e. require only a small reverse magnetic field to demagnetise, while hard ferrites show both large remnant magnetisation and coercive force. Soft ferrites consequently show little hysteresis loop loss and are used for example in transformer cores while hard ferrites show large hysteresis loop loss and consequently make good permanent magnets.

It is known that some soft ferrites can be made by pressing at elevated temperatures coprecipitated mixtures of hydroxides which are precursors of the oxides required to produce the ferrite[4]. It has been shown that such a technique, technically called reaction hot pressing or sometimes, reactive hot pressing, is able to produce oxides which are partially crystallographically oriented spontaneously by the process if the oxide is anisotropic in its crystal properties[5]. Other work[6,7] indicated that water vapour plays some role in the overall reaction pressing process.

It has been demonstrated that differential thermal analysis (DTA) can be performed during reaction hot pressing and the results used in an attempt to explain the overall process[5]. The production of lead hexaferrite from coprecipitated lead carbonate and hydrated ferric oxide has been shown to occur at temperatures as low as 700°C (ref. 8). This is in reasonable agreement with the known phase diagrams for the lead oxide–iron oxide system[9,10]. Lead hexaferrite, having the magnetoplumbite crystal structure, is hexagonal in its crystal habit and therefore anisotropic in its properties[1] and is a good permanent magnet material.

With the above literature in mind, it was proposed that partially oriented lead hexaferrite should be produced at moderate temperatures by the reaction hot pressing of coprecipitated mixtures of lead carbonate and hydrated ferric oxide. It was hoped that DTA could be carried out on a reacting sample during the pressing procedure.

EXPERIMENTAL EQUIPMENT AND PROCEDURE

The mold assembly and press is represented in Fig. 1. The press is a hydraulic hand operated laboratory press. The mold body is of 316 stainless steel while plungers are of Inconel 610. The furnace is a nichrome wound resistance furnace providing a heating rate of about 8°C min^{-1}. Temperature of the mold was monitored with a Pt/Pt–13% Rh thermocouple and a 0–10 mV full scale strip chart recorder. Temperatures are accurate to ±3°C. The actual DTA cell is shown in Fig. 2. Early experiments using the mold itself as a reference showed that the DTA system was pressure sensitive and gave inconsistent results. The cell shown in Fig. 2 was consequently designed and tested. It shows no detectable pressure sensitivity. This improvement is thought to be due to both sample and standard being at the same pressure. Because of the nature of the DTA couple it was necessary to rebuild it for each experiment.

Each experiment consisted of charging the "sample" cavity with a known weight of the material under test and the "standard" cavity with strontium hexaferrite [$SrFe_{12}O_{19}$][*]. A hexaferrite was used to closely approximate the thermal

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[*] For details of experimental production of test starting materials see refs. 8, 11.

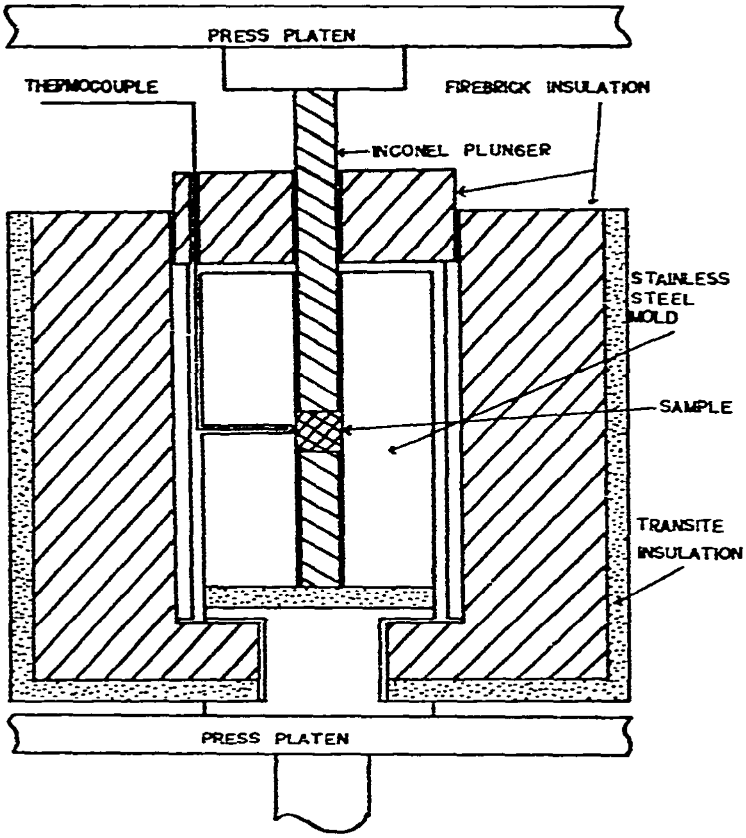

Fig. 1. Schematic representation of the hot pressing apparatus.

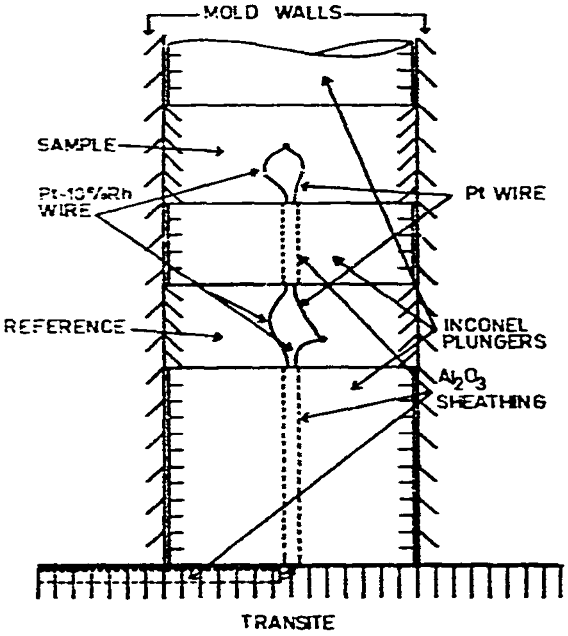

Fig. 2. The DTA cell arrangement employed during the full range hot pressing runs.

conductivity of the expected product in the tested sample, and strontium hexaferrite was chosen for its lack of thermal activity in the test temperature range plus convenience of manufacture[12]. Once the charging and assembly was accomplished the system was pressurised to the required experimental pressure and held there for the duration of the experiment. The furnace was turned on at this point and the temperature thermocouple and DTA couple outputs recorded up to the desired maximum value of temperature.

Simultaneous compaction data were also obtained during the experiments. Specimens produced were further evaluated by X-ray diffraction for product identification, by mercury balance for density, and by various magnetic methods to determine coercive force, remnant magnetisation, maximum energy product, and magnetic moment per gram.

RESULTS

DTA traces for the lead and iron components of the precipitate, a baseline for Al_2O_3 vs. $SrFe_{12}O_{19}$ (standard) and a series of different applied pressure experiments are shown in Figs. 3, 4, 5, and 6, respectively. A composite curve for a "non reacting" mixture of precipitated components is given in Fig. 7. This is produced by impressing on the baseline the thermal activity of the two precipitated components weighted to the correct stoichiometry and total weight from the individual thermal behaviour of the components. Figures 8 and 9 show the DTA adjusted results produced by subtracting the curve in Fig. 7 from the curves in Fig. 6. It should be noted here that the same curve (Fig. 7) was subtracted in all cases as it was found that the curves in Figs. 3–5 showed no sensitivity to pressure.

DISCUSSION

The curve in Fig. 3 reveals that the lead is probably present in the coprecipitate in the form of basic lead carbonate. The DTA of the hydrated ferric oxide component

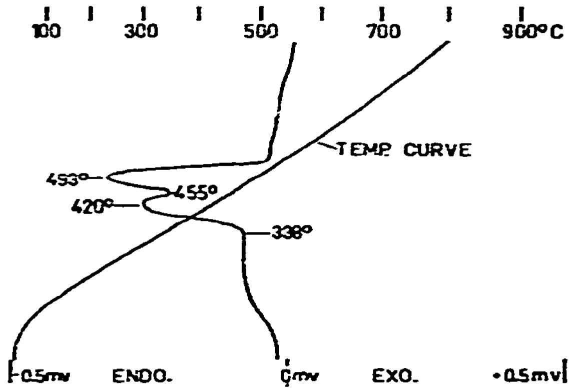

Fig. 3. DTA for the lead component of the coprecipitate (0 applied pressure).

of the coprecipitate did not show any evidence of the γ to α transformation in Fe_2O_3. This is supported by a lack of γ-Fe_2O_3 lines in the X-ray diffractograms for all samples studied. No sharp evidence of the Néel point of α-Fe_2O_3 at about 680°C was seen in either pure hydrated oxide samples or reacting coprecipitates, although a possible exothermic trend can be seen at 670°C in Fig. 4 .Normally the Néel point (spontaneous change from antiferromagnetic to paramagnetic behaviour) is indicated by a sharp exotherm.

What is evident from Figs. 8 and 9 is that there are two consistent areas of exothermic activity in the "corrected" traces for all experimental pressures. These are labelled A and B. The peak temperatures for A and B are plotted against applied pressure in Fig. 10.

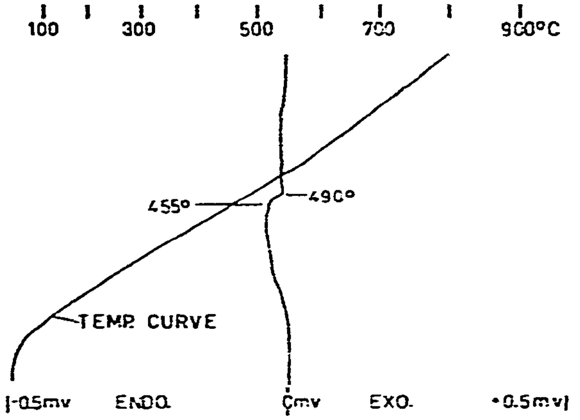

Fig. 4. DTA of the iron component of the coprecipitate (0 applied pressure).

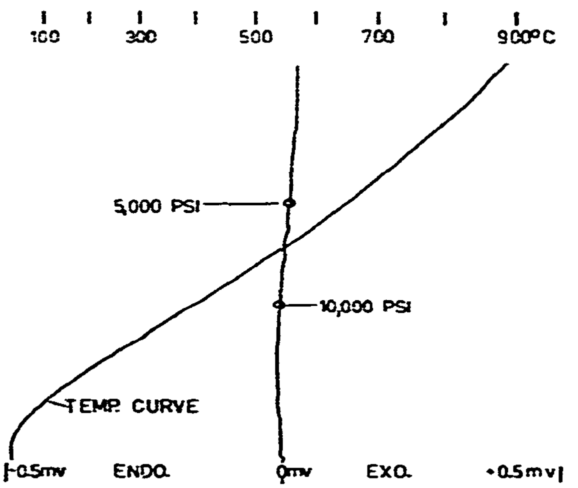

Fig. 5. DTA of an Al_2O_3 sample with $SrFe_{12}O_{19}$ as the reference material (5,000 psi applied pressure). Pressure varied at several points as indicated.

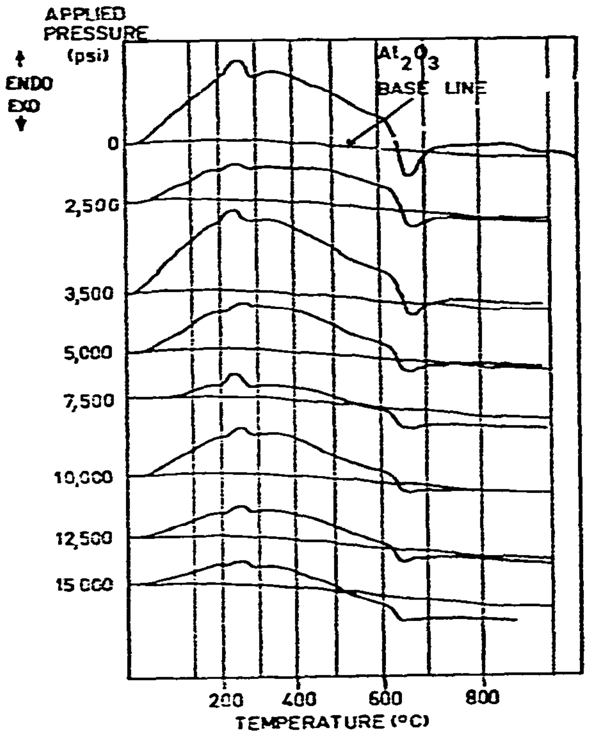

Fig. 6. DTA traces of the coprecipitate at various values of the applied pressure ($SrFe_{12}O_{19}$ reference).

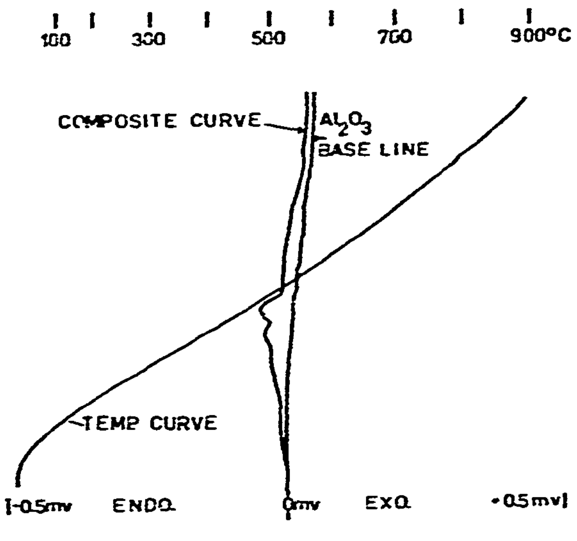

Fig. 7. The composite "non-reacting mixture" curve (DTA) prepared from Figs. 3–5 as described in the accompanying text.

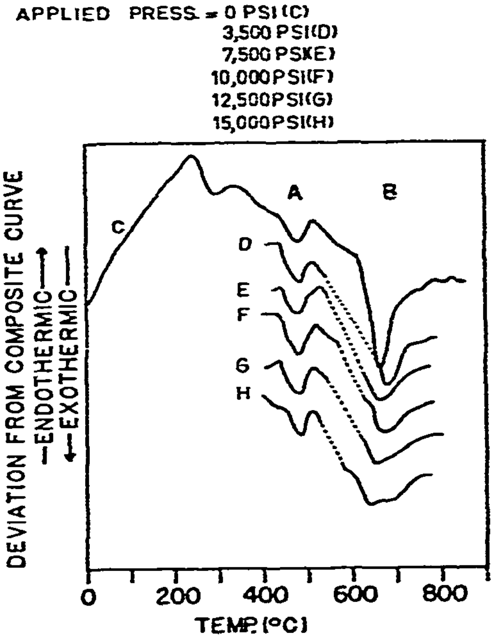

Fig. 8. Deviations of sample DTA curves from the "non-reacting mixture" curve of Fig. 7 at various values of the applied pressure.

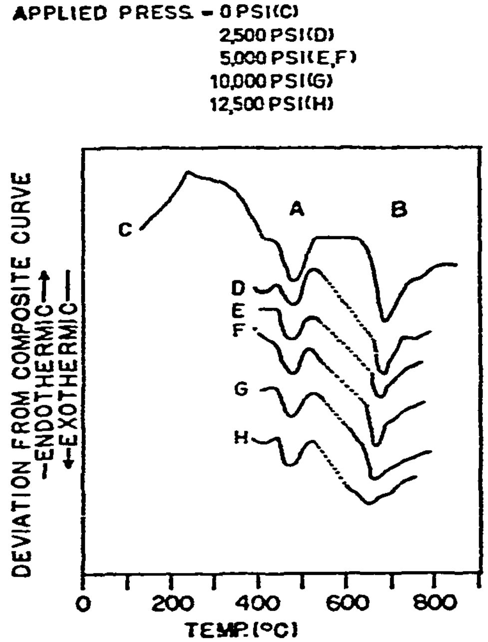

Fig. 9. Deviations of the sample DTA curves from the "non-reacting mixture" curve of Fig. 7 at various values of the applied pressure. The samples are from a different batch of the coprecipitate than those in Fig. 6.

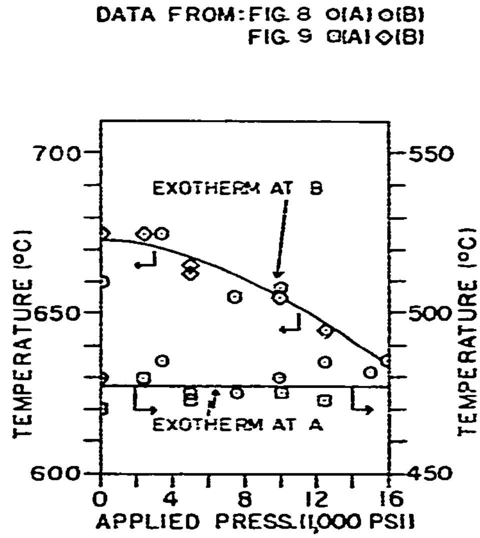

Fig. 10. Temperatures of the maximums in the exothermic trends in Figs. 8 and 9 vs. the applied pressure.

It can be seen that event A is pressure insensitive. It is unlikely that this feature is a function of the process of subtracting the "composite baseline", as if it were, one would expect that the event would occur at about 490°C where in fact it appears to be at about 475°C. It is thought that this event is associated with the destruction of surface area by recrystallisation of iron oxide in the presence of water vapour. X-ray diffractograms indicate a large increase in crystallite size in specimens heated under 10 000 psi applied pressure to 500°C as compared to 400°C.

The exothermic event labelled B can be seen indistinctly in the data in Fig. 6 and clearly in Figs. 8 and 9. The data plotted in Fig. 10 clearly show that this event is strongly pressure-sensitive. The most obvious explanation of this event is the formation of an iron oxide–lead oxide compound. It is known from experimental X-ray and magnetic data that lead hexaferrite is present in samples pressed at temperatures above 600°C, however, lead hexaferrite should not form until at least 740°C according to the published PbO–Fe_2O_3 phase diagrams[8,9]. On examining the published phase diagrams one can see that at about 650 to 670°C 2PbO·Fe_2O_3 should form from PbO–Fe_2O_3 mixtures. Considering that the change in volume for unit weight of a 1:6 PbO:Fe_2O_3 mole ratio is −1.06% for Fe_2O_3 plus 2PbO·Fe_2O_3 production compared to +0.87% for the production of hexaferrite then one would expect 2PbO·Fe_2O_3 to form first on the basis of ΔPV considerations. (These figures are based on initial PbO as litharge $\rho = 9.53$. They become −3.37% and −2.22%, respectively, based on PbO as massicot $\rho = 8.0$). Because of the volume reduction associated with the reaction one would expect that the reaction would be pressure-sensitive, the reaction occurring at a lower and lower temperature at increasing applied pressure values. This would then suggest that the formation of lead hexaferrite in the system occurs via the formation of, and subsequent reaction with ferric oxide of, $2PbO \cdot Fe_2O_3$. This mechanism is not supported by X-ray data. This is not surprising since in a mechanical mixture of $2PbO \cdot Fe_2O_3$, $PbFe_{12}O_{19}$ and Fe_2O_3, where 25% of the PbO is in the $2PbO \cdot Fe_2O_3$ form, no evidence of $2PbO \cdot Fe_2O_3$ can be seen in X-ray diffractograms. X-ray diffractograms from horizontally cleaved specimen surfaces show evidence of crystallographic alignment for high temperature, high pressure experimental conditions.

CONCLUSIONS

Corrected DTA results for reacting mixtures in which the thermal effects associated with changes in the mixture components are subtracted from overall behaviour can be used to examine the reaction alone.

Using this technique together with auxiliary data, it has been possible to identify two separate thermal events in the production of partially oriented high density lead hexaferrite magnets by reaction hot pressing of coprecipitated basic lead carbonate and hydrated ferric oxide.

The exothermic event at about 475 °C is likely due to the increase in crystallite size of iron oxide in the mixture. This increase is due to the "mineralising" effect of trapped water vapour. This event is pressure insensitive. The exothermic event at between 675 and 635 °C over the applied pressure range 0 to 15 000 psi is ascribed to the onset of formation of lead oxide–iron oxide compounds, initially $2PbO \cdot Fe_2O_3$. This agrees well with reported literature.

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