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Short communication

Thermomagnetometric evidence of γ-Fe_2O_3 as an intermediate in the oxidation of magnetite

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Abstract

The oxidation of magnetite, Fe_3O_4, to hematite, α-Fe_2O_3 was followed by thermogravimetry (TG), both with and without a small magnetic field gradient imposed upon the sample. The results of this thermomagnetometry (TM) clearly indicates the formation of a strongly magnetic intermediate during the oxidation process. This intermediate reaches a maximum concentration at about 270 °C and disappears by approximately 320 °C. This confirms the speculation that γ-Fe_2O_3 is as an intermediate in this oxidation process [J. Therm. Anal. Calorim. 73 (2003)].

Keywords: Thermogravimetry; Oxidation; Magnetite; Thermomagnetometry

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1. Introduction

The oxidation of magnetite (Fe_3O_4) to hematite (α-Fe_2O_3) has been described as proceeding through the formation of γ-Fe_2O_3 as a metastable intermediate, both for precipitated [1,2] and coarse [3] starting materials. A recent study [1] of the kinetics of the overall oxidation process using simultaneous thermogravimetry (TG) and differential scanning calorimetry (DSC) revealed the influence of this intermediate formation on the kinetic mechanism. Since the metastable to stable (γ to α) conversion process does not involve a change in mass, TG does not directly reflect this transformation. The conversion, however, does evolve heat and therefore, does influence the kinetics as observed by DSC.

Because γ-Fe_2O_3 is strongly magnetic, the formation of the intermediate and its metastable conversion process should become evident by comparing the results of TG and thermomagnetometry (TM) for the overall oxidation process. It was speculated in the previous kinetic study [1] that the metastable conversion process was completed before all of the magnetite was oxidized and thus the final step in the overall process was the direct oxidation of magnetite to hematite without the formation of the intermediate. Again, a comparison of the TG and TM curves should be able

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to confirm that speculation. This note describes such a comparison.

2. Experimental procedures and results

The starting material and instrumentation were the same as that used in the earlier kinetic study [1]. The source of magnetite was Alpha, Puratronic grade. Three pairs of TG and TM experiments were performed using closely paired weights in the range from 11.7 to 20.2 mg. The atmosphere was flowing 20% O_2 in N_2 at a rate of $1.0\,\mathrm{l\,min^{-1}}$. The heating rate was nominally $16\,\mathrm{K\,min^{-1}}$. The materials were heated to 800 °C to ensure complete oxidation.

TG studies were performed with a Netzsch Model 449C TG/DSC instrument using its Rh furnace. Samples were contained in the manufacturer's alumina crucibles. Small permanent magnets supplied by Netzsch were used during the TM experiments. The magnets were arranged outside the furnace in a fashion that the magnetic field gradient pulled upward on the sample and therefore, gave rise to an apparent loss in sample mass for a magnetic material. The TG and TM baselines were corrected by subtraction of predetermined baselines run under identical conditions except for the absence of sample.

Fig. 1 shows the results for one of the pairs of TG and TM experiments. The ordinate is percentage weight gain and the slight offset at the end of the experiment is due to the small difference in the starting sample weights. The initial magnetic offset and that through the course of the reaction reflects the magnetic attraction upon both the remaining magnetite and the magnetic intermediate. The final product is antiferromagnetic with only a trivial attraction at this sensitivity.

The TM curve is subtracted from the TG curve for the same pair as shown in Fig. 1 using the Netzsch software and the resulting difference is displayed in Fig. 2. Results for all three pairs were very similar and, had a peak in the ΔW (differential weight) curve at

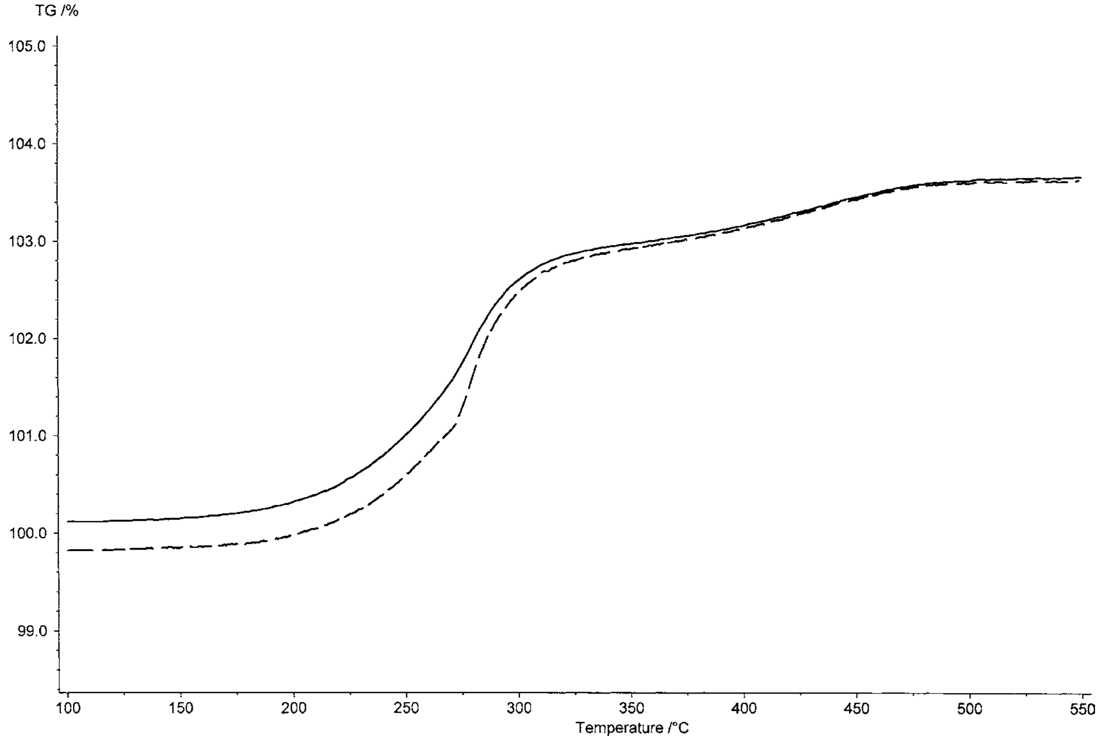

Fig. 1. TG and TM curves for the oxidation of magnetite in 20% O_2/80% N_2 at a rate of $16\,\mathrm{K\,min^{-1}}$. (—) TG, 11.9 mg; (- - -) TM, 11.7 mg.

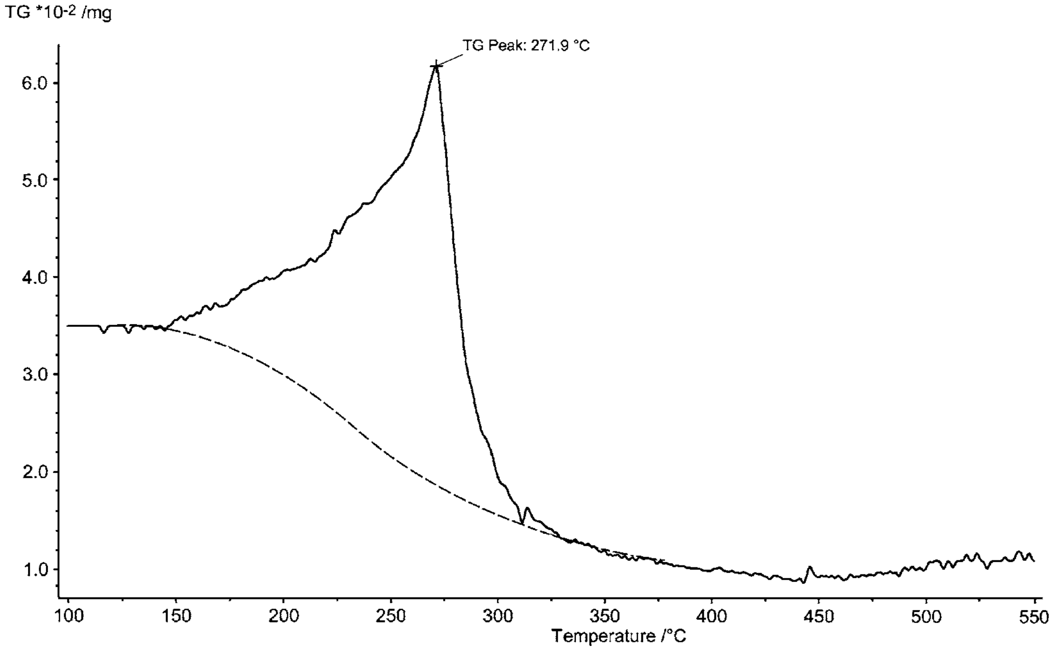

Fig. 2. (—) Subtraction curve, TG and TM, derived from Fig. 1. (- - -) Simulated curve in the absence of the intermediate.

temperatures in the remarkably narrow range of 270–272 °C. Again the slight offset at the final temperature is due to the small difference in the initial weights.

3. Discussion

The conclusions are best derived by focusing on Fig. 2. The initial offset of about 30 μg below 100 °C represents the attraction of the magnetic field on the starting sample of magnetite. As the oxidation proceeds, the value of ΔW is observed to increase sharply up to 272 °C before it begins to drop off. The difference between the two curves, however, should decrease smoothly and ultimately merge if the there was no formation of a magnetic intermediate. Clearly, a magnetic intermediate is being formed initially. It would appear that the intermediate must be more magnetic than the magnetite itself, but this is not necessarily true. Since the intermediate is formed in the presence of the magnetic field gradient, the nuclei and subsequent growth would be expected to be aligned with the field better than essentially random distribution of domains present in the original sample.

Near 270 °C, the magnetic and metastable γ-Fe_3O_3 begins to revert to the stable α-Fe_3O_3, which although it produces no change in mass does lead to an apparent change in weight associated with the loss of magnetic attraction. When all of the γ-Fe_3O_3 has converted, the TM curve should revert to the simple TG curve. This appears to occur around 325 °C. The dashed section in Fig. 2 represents a simulation of the TM curve that had there been no formation of the intermediate.

The disappearance of the intermediate around 325 °C agrees well with the plateau and obvious change in mechanism observed in both the TG and DSC studies of the kinetics. The conclusions based on this brief thermomagnetometric investigation seem to confirm the speculations derived from an earlier paper describing the kinetics of the overall process.

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