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Isothermal Thermal Diffusivity of Iron Oxide

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Using the flash technique, the thermal diffusivity of iron oxide has been measured as a function of time at temperatures ranging from 623 to 753 K to study the isothermal decomposition of wustite to magnetite and iron. The results are briefly discussed in terms of transformation kinetics and it is shown that the data are consistent with the growth of a fixed number of nuclei, all of which are present at the start of transformation.

KEY WORDS: thermal diffusivity; iron oxide; isothermal decomposition.

1. INTRODUCTION

Measurements of thermal diffusivity have, over the past two decades, proved an increasingly popular method of generating basic thermal transport property data. Although an important parameter in its own right, thermal diffusivity (α) is simply related to thermal conductivity (λ)

$$\lambda = \alpha C_P \rho$$

Hence, provided that density (ρ) and specific heat (C_P) are known, thermal diffusivity measurements, which can usually be made in a short time, provide a potentially attractive method whereby thermal conductivity data may be obtained. However, in situations where kinetic changes are occurring, thermal conductivity measurements will merely yield a steady-state resultant value when all changes are complete. It has been postulated that such changes can be monitored as they occur by repeated diffusivity measurements. This

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paper details just such an investigation in which the decomposition of wustite to magnetite and iron

$$4FeO \rightleftharpoons Fe_3O_4 + Fe$$

is studied over the temperature range 623–753 K. This is the first instance known to the authors where an isothermal transformation has been studied using a thermal transport property measurement.

2. THERMAL DIFFUSIVITY APPARATUS

The theory of the "flash" or heat pulse has been adequately detailed in many published works [1,2], so the method will not be reviewed here. In the apparatus at the University of Manchester, the heat pulse is supplied by a solid state ruby laser (wavelength = 0.65 μm) of duration $\sim 10^{-3}$s. The specimen of 10 mm diameter and of a thickness governed by the diffusivity of the material, is heated to the measurement temperature inside a graphite susceptor using an induction coil. Within the temperature range covered by this investigation, the temperature change with time of the opposite face of the specimen is monitored using a lead sulphide detector. The amplified output of the detector is recorded and analyzed using a computer. Further details of the apparatus are outlined in another paper [3].

3. SPECIMEN DETAILS

An investigation has been carried out to determine the thermal diffusivity of oxide layers formed on iron, iron alloys, and steel. In order to produce suitable specimens, unilateral oxide scales were produced on 1 cm. diam 1 mm thick disk samples by exposing the top face to an atmosphere of high purity argon containing 0.001% oxygen in a specially constructed oxidation facility [4]. For adherent oxide layers so produced, the diffusivity of the oxide was calculated using two-layer heat flow analysis [5]. Preliminary measurements in this investigation have been previously reported [6].

It is known that, according to the iron oxygen equilibrium diagram, wustite undergoes a eutectoid transformation to magnetite and iron at 838 K [7]. Evidence of this transformation was observed in iron oxide layers produced by unilateral oxidation. Initially during heating, the thermal diffusivity was roughly constant or increasing slightly over the temperature range 550–750 K. Then over the temperature range 750–875 K, the diffusivity decreased markedly and then remained roughly constant at this value during further heating to 1350 K. Significantly, however, measurements taken during cooling to 450 K showed the diffusivity to be fairly constant, with no increase in diffusivity below 838 K. It may be postulated, therefore, that the decomposition of wustite is a fairly sluggish, time dependent process, which does not proceed to completion during the time scale over which diffusivity measurements are made during cooling. This, it must be added, is significantly faster than the very slow cooling rates necessary to maintain oxide adherence following unilateral oxidation.

Investigation of this phenomenon using thin adherent oxide layers (0.05–0.2 mm thick) would prove difficult. Therefore, a thicker oxide layer was produced on a pure iron sample by oxidizing for a longer time at a higher temperature, namely 6 h at 1148 K. This produced an oxide layer 0.35 mm thick, which could be detached from the iron substrate and was sufficiently robust to handle. Thermal diffusivity measurements on this sample (Fig. 1) (over the temperature range 450–1250 K) confirmed the measurements already made on two-layer samples.

4. EXPERIMENTAL DETAILS

The specimen was placed in the thermal diffusivity apparatus and homogenized for 45 min at 1075 K to produce a fully wustite structure. After each homogenization anneal, it was rapidly cooled to the isothermal measurement temperature. Isothermal diffusivity measurements were taken at each of four temperatures: 623, 693, 723, and 753 K. The cooling times were of the order of 5 min. Diffusivity measurements were taken at not less than 3 min

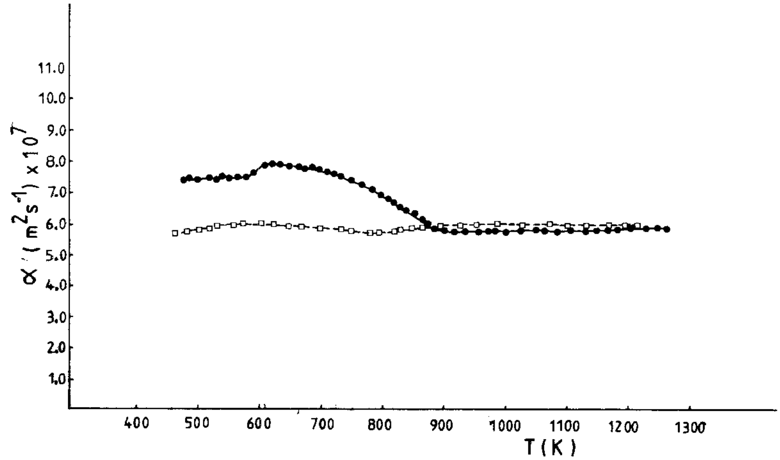

Fig. 1. Thermal diffusivity versus temperature for a sample of iron oxide (L = 0.35 mm). -●-, heating; --□--, cooling.

Table I. Summary of Data on Time Dependence of Diffusivity Changes

T(K)	Initial diffusivity $\alpha_0 \times 10^7 m^2 s^{-1}$	Final diffusivity $\alpha_t \times 10^7 m^2 s^{-1}$	Time to completion t (min)
753	5.82	8.47	604
723	6.01	8.90	225
693	6.15	9.80	195
623	6.20	9.55	300

intervals (this being the time required for the computer to complete a calculation), until no further change in diffusivity was observed.

5. RESULTS

The results are summarized in Table I, which shows a number of interesting features. There is a marginal increase in initial thermal diffusivity, the lower the isothermal temperature. Over the temperature range 753–693 K, the time required for the diffusivity to reach a maximum decreases as the temperature is lowered, and the resultant final diffusivity is also higher. However, for the anneal at 623 K, a lower maximum diffusivity is observed, and the time for changes to occur is also longer than either the 693 or 723 K anneals. These observations are broadly in agreement with the heating curve depicted in Fig. 1. In Fig. 2, the fractional increases in thermal diffusivity ($\alpha_t - \alpha_0$) are plotted as a function of time.

The reaction kinetics of sigmoidal rate curves of this type may be

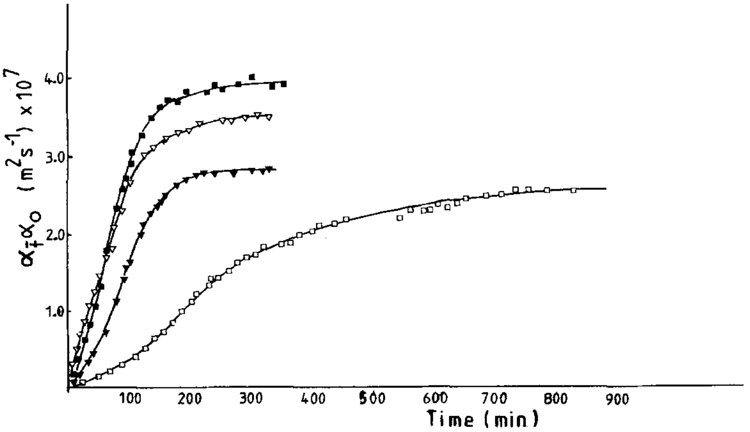

Fig. 2. Increase in thermal diffusivity ($\alpha_t - \alpha_0$) as a function of time, t. ▿, 623 K; ■, 693 K; ▾, 723 K; □, 753 K.

analyzed empirically by an equation of the form

$$\partial y/\partial t = k^n t^{n-1}(1-y) \tag{1}$$

where $(1-y)$ is generally regarded as an allowance for the retardation in reaction rate due to impingement, k and n are constants, and y is the fraction transformed. Integrating this equation yields

$$\ln\left(\frac{1}{1-y}\right) = (kt)^n \tag{2}$$

and plots of loglog $[1/(1-y)]$ versus log$t$ yield a straight line of intercept k and slope n. This is frequently referred to as the Johnson-Mehl equation, since those authors used an equation of this form with $n = 4$ for the special case of the formation of pearlite from austenite [8].

Rigorous treatments of precipitation kinetics show that this relationship only holds up to approximately 50% transformation [9,10]. Experimentally determined nucleation curves usually increase linearly up to a maximum corresponding to 40–70% transformation and thereafter decrease.

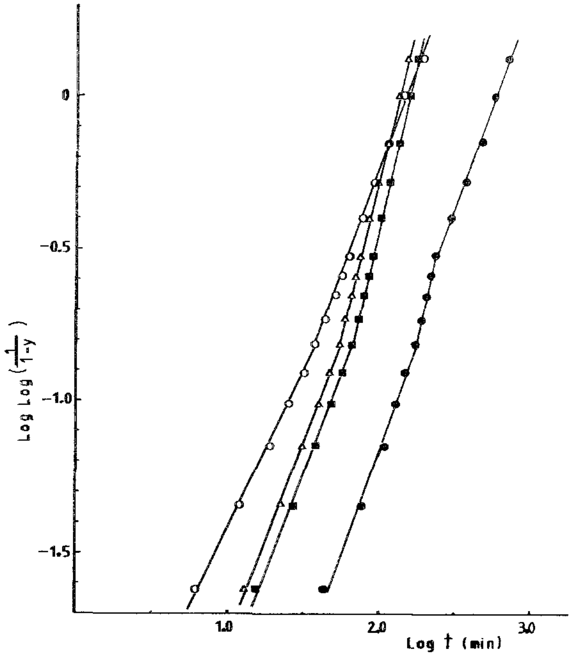

Fig. 3. Data plotted according to loglog equation $\ln[1/(1-y)] = (kt)^n$. ○, 623 K; △, 693 K; ■, 723 K; ●, 753 K.

Table II. Isothermal Transformation Kinetic Data

T(K)	Range of y	n	k (s^{-1})
753	0–0.25	1.36	4.2×10^{-5}
	0.25–0.5	1.96	5.8×10^{-5}
	0.5–0.95	1.25	5.1×10^{-5}
723	0–0.25	1.25	10.5×10^{-5}
	0.25–0.95	2.12	15.4×10^{-5}
693	0–0.25	1.25	12.5×10^{-5}
	0.25–0.75	2.12	19.0×10^{-5}
623	0–0.25	1.05	16.0×10^{-5}
	0.25–0.95	1.47	20.4×10^{-5}

Plots of $\log\log[1/(1-y)]$ versus log time are presented in Fig. 3. The curves are linear up to 25–30% transformation, and thereafter exhibit an enhancement of the reaction rate as shown by the increase in slope of the curve. Data on the transformation kinetics deduced from these curves are summarized in Table II. From these data, attempts to derive an activation energy from Arrhenius plots were unsuccessful, as plots of log time to a given percentage of transformation versus T^{-1} were strongly curved.

6. DISCUSSION

Although the data have been analyzed using equations appropriate to isothermal transformation kinetic studies, it is dangerous to attempt to draw any detailed conclusions. Primarily, this is because each individual thermal diffusivity measurement involves a temperature excursion through the sample. Although the rear face temperature rise T_M may be limited to 2–3 degrees, and the average temperature rise may be 1.6 times this value, there is a substantial energy input to the front face of the sample. The front face temperature rise T_f is proportional to $T_M\ L/\alpha^{1/2}$, which, since T_M is usually governed by equipment sensitivity, means that T_f can be substantial for low diffusivity materials. In the particular situation of this sample, T_f could be as high as 50 K. Hence only tentative general conclusions may be drawn.

Nevertheless, the data up to 25% transformation show values of the time exponent n ranging from $1.05 < n < 1.36$. These values are reasonably consistent with the predicted value of $3/2$ for diffusion controlled growth of a fixed number of crystals, provided shape does not change with growth, for which all nuclei are present at the start of transformation [11]. The acceleration of the decomposition process beyond 25%, as evidenced by the higher values of n, is relatively uncommon. Nevertheless, overall the results appear to support the view that the eutectoidal decomposition of wustite is a two-stage process. At temperatures below 753 K, it is believed that the initial stage of the nucleation and growth of a magnetite precipitate occurs more slowly than the final stage, in which iron and the additional magnetite probably form simultaneously. The slower growth kinetics at 623 K are predictable. At 753 K, however, the eutectoid reaction involves an initial precipitation of iron, and the present results suggest that the remainder of the transformation may occur in two distinctive stages. The first stage is a more rapid precipitation of magnetite from the oxygen enriched areas of the wustite, and the second stage is a slower final precipitation of additional iron and magnetite. It is the latter stage that may account for the longest overall transformation time indicated in Table I. This result contrasts with the earlier view [12] that the most rapid transformation occurs around 753 K. Table I shows that the shortest transformation time occurred at 693 K, for which the final thermal diffusivity reached a maximum.

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