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Letter

Diffusion of nitrogen in R_2Fe_{17} (R = rare earth) compounds determined by the Kissinger method

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Abstract

The activation energy of nitrogen diffusion in R_2Fe_{17} (R = rare earth) compounds has been determined by applying the Kissinger method to analyse the differential scanning calorimetry (DSC) traces of nitrogenated R_2Fe_{17} compounds. The nitrogen outgas that starts when the nitrides are heated above about 300 °C is a typical decomposition reaction of the type solid → solid + gas to which the Kissinger method can be applied. From the heating-rate dependence of the endothermic peaks in the DSC curves, values for the activation energy of nitrogen diffusion are derived. There is good agreement between the results for Sm_2Fe_{17} and Nd_2Fe_{17} obtained in the present investigation and the results reported in the literature which were obtained by means of other methods.

Keywords: Diffusion; Nitrogen; Kissinger method; Differential scanning calorimetry

1. Introduction

Gas–solid nitrogenation of rare earth (R)–transition metal (T) compounds is realized via the adsorption of molecular nitrogen on the surface of the particles, dissociation of these N_2 molecules and diffusion of nitrogen atoms into the particles. In order to understand the nitrogenation processes and to obtain sufficiently nitrogenated samples, it is important to know more about the diffusivity of nitrogen atoms in the R–T compounds.

The diffusion of a substance A into substance B can be described by expressing the mean squared displacement of an atom in the x direction by

$$\langle x^2 \rangle = 2Dt \tag{1}$$

where D is the diffusion coefficient and t the diffusion time. D is expressed by

$$D = D_0 \exp(-E/RT) \tag{2}$$

where D_0 is called a frequency factor, E is the activation energy, T the temperature and R the gas constant. Clearly, the activation energy must be determined in order to understand the diffusion process.

Since the beginning of the worldwide study on interstitial R–T nitrides, much effort has been devoted to investigations of the diffusion of nitrogen in R_2Fe_{17} compounds. Coey et al. [1] estimated the diffusion coefficient of nitrogen in Sm_2Fe_{17} by measuring the diffusion time in powder particles of known size, and reported a value of the activation energy equal to 78 kJ mol^{-1}. Later, Coey and coworkers determined the activation energy as 133 kJ mol^{-1} by thermopiezic analysis of the initial stage of nitrogen uptake, using the lattice gas model [2–4]. Kanneko et al. [5] measured the activation energy as 66.1 kJ mol^{-1} by analysing the depth profile of N in Sm_2Fe_{17}, using glow discharge spectroscopy as a function of time and temperature. Uchida and coworkers [6–8] determined the activation energy to be in the range 100–163 kJ mol^{-1} by measuring the depth of the N layers in Sm_2Fe_{17} samples. Colucci and coworkers [9–12] studied the diffusion patterns of nitrogen also in Nd_2Fe_{17} and found that the diffusion of interstitial nitrogen atoms in the bulk at 500 °C is competitive with the faster diffusion along the defects in the particles.

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All the determinations of the activation energy mentioned above are based on measurements or estimates of the parameters contained in Eq. (1). These measurements, however, are often difficult and time consuming. There is an alternative method for determining the activation energy quickly by measuring the endothermic peak positions accompanying nitrogen outgassing. This method was developed by Kissinger in 1957 [13], when studying the kinetics of reactions of the type solid→solid′+gas. This is the type that perfectly fits the situation of nitrogen outgassing during heating the interstitial compounds. In this section, we will study the diffusion of the interstitial nitrogen in R_2Fe_{17} compounds by means of the Kissinger method.

2. Experimental procedure

The Kissinger method was established originally for determining the activation energy of decomposition reactions in solids. This kind of reaction is accompanied by a heat effect, which can be detected by differential thermal analysis or differential scanning calorimetry (DSC) as peaks in the temperature scans. The heat effect of the N_2 outgassing of Nd_2Fe_{17} and Sm_2Fe_{17} nitrides with particle sizes less than 40 μm was measured using Perkin-Elmer DSC-7 equipment. The outgassing of nitrogen from the R_2Fe_{17} nitrides takes place in a rather wide temperature range, starting from about 300 to about 700 °C. Therefore, in the DSC traces usually no sharp peaks of the outgassing process can be measured and only the endothermic effect like that shown in Fig. 1 can be found.

The situation can be changed, however, by varying the experimental conditions, especially the atmosphere in the sample chamber. In our case, flowing argon gas was used. When the flow rate is chosen smaller, the heat effect due to the outgassing becomes more pronounced. Fig. 2 shows the endothermic peaks of the outgassing of nitrogen from the Nd_2Fe_{17} nitride with different heating rates. In all cases, the peaks are quite sharp, and the peak positions T_m are well defined.

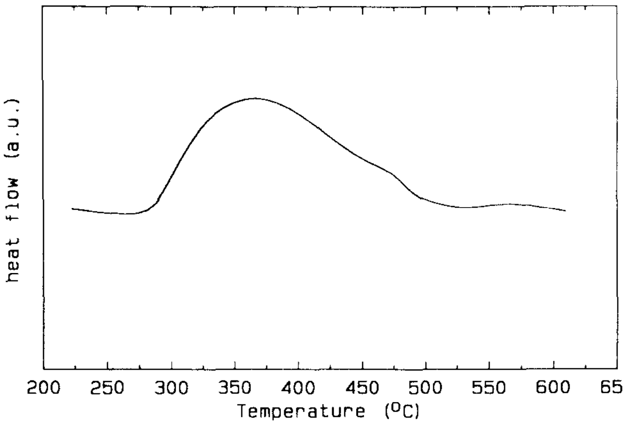

Fig. 1. The usual situation of the DSC traces of the nitrides. The heating rate for this curve is 20 °C min^{-1}.

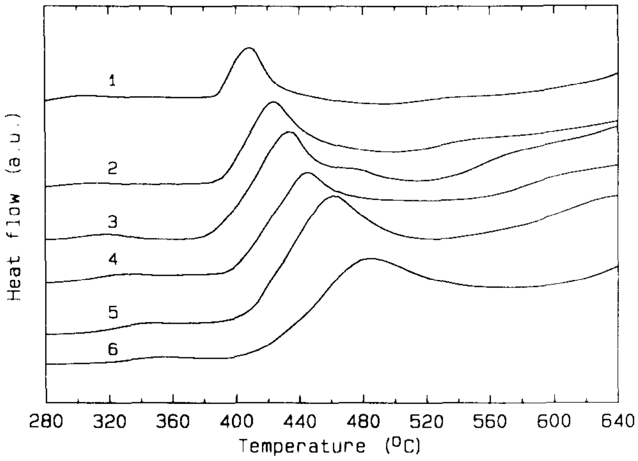

Fig. 2. The endothermic peaks of the nitrogen outgas measured on $Nd_2Fe_{17}N_{2.7}$ for heating rates of 5 °C min^{-1} (curve 1), 10 °C min^{-1} (curve 2), 15 °C min^{-1} (curve 3), 20 °C min^{-1} (curve 4), 30 °C min^{-1} (curve 5) and 50 °C min^{-1} (curve 6).

3. Results and discussion

From Fig. 2 one can see that there is a clear dependence of the peak position on heating rate. The faster the heating, the higher the peak temperature. By measuring the dependence of T_m on the heating rate ϕ, the activation energy can be determined through the relation [13]

$$\frac{d[\ln(\phi/T_m^2)]}{d(1/T_m)} = -\frac{E}{R} \tag{3}$$

When the outgassing is controlled by one single thermally activated process, one expects a linear dependence of ln (ϕ/T_m^2) on $1/T_m$ with a slope equal to E/R. Fig. 3 shows plots of $\ln(\phi T_m^2)$ against $1/T_m$ measured in the outgassing of $Nd_2Fe_{17}N_{2.7}$. The results shown in the figure make it clear that the outgassing can hardly be described by one single thermally activated process. Rather, the results suggest that there are essentially two different processes, corresponding to two different regimes. From the slope of the two straight lines, values for the corresponding activation energies were determined. These values are 59 and 144 kJ mol^{-1}. Similar measurements were also made on $Sm_2Fe_{17}N_x$; the two activation energies of N diffusion in $Sm_2Fe_{17}N_x$ compound are 64 and 168 kJ mol^{-1}. These values are in very good agreement with the result obtained by Uchida and coworkers [6–8]. The latter value of 168 kJ mol^{-1} is a typical value for the interstitial diffusion of gas atoms in a metal [14], whereas the former value of 64 kJ mol^{-1} is in good agreement with the activation energy reported by Kanneko et al. [5].

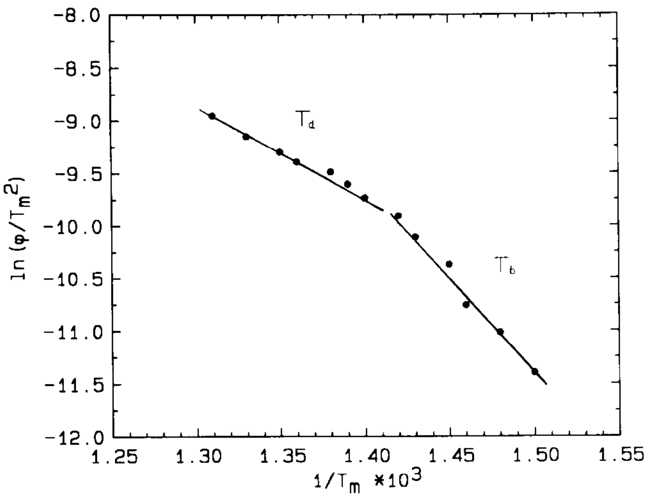

Fig. 3. Plots of $\ln(\phi/T_m^2)$ vs. $1/T_m$ for $Nd_2Fe_{17}N_{2.7}$. The lines are guides to the eye.

It is tempting to interpret the two types of diffusion processes as follows. As has been mentioned above, the activation energies of 168 kJ mol^{-1} for $Sm_2Fe_{17}N_x$ and 144 kJ mol^{-1} for $Nd_2Fe_{17}N_x$ are typical values for bulk diffusion proceeding via interstitial sites. We suggest that the lower values (64 kJ mol^{-1} for $Sm_2Fe_{17}N_x$ and 59 kJ mol^{-1} for $Nd_2Fe_{17}N_x$) correspond to the diffusion of nitrogen atoms along defects in the particles.

It is well known that a lot of defects are produced in powder particles upon pulverization, comprising dislocations and vacancies. In this connection, it is also important to pay attention to the fact that in R_2Fe_{17} compounds stacking faults can be easily formed already during casting [15]. Therefore, it is reasonable to suppose that nitrogen will diffuse along the defects of high density in the R_2Fe_{17} particles with lower activation energy than that needed for the bulk diffusion.

Large mass transport along the defects only occurs if there is enough supply of atoms from the interior of the grain (we assume that the contribution of N atoms located already along the defects is relatively unimportant). This means that a substantial thermal effect due to the diffusion along the defects will occur only if it occurs simultaneously with bulk diffusion. In terms of the DSC traces this means the endotherm due to mass transport along the defects has to coincide or to be preceded by the bulk diffusion endotherm in order to be observable. The activation energy for diffusion along the defects is much lower than that for bulk diffusion. Therefore, the endotherm due to diffusion along the defects will shift more strongly to higher temperatures with increasing heating rate than the endotherm due to bulk diffusion. As will be discussed below, this leads automatically to the two diffusion regimes observed in our DSC measurements.

For low heating rates, the thermal effect of diffusion along the defects is expected to occur at temperatures lower than the thermal effect due to bulk diffusion. Due to lack of supply of N atoms it will not be observed, meaning that the endotherm of the corresponding DSC traces represents bulk diffusion. The heating rate dependence of the endotherm in this range is fairly slow and characterized by a comparatively high activation energy (regime T_b in Fig. 3 with $E = 144$ kJ mol^{-1}). It is good to realize that sufficient mass transport from the interior of the particles to the gas phase becomes possible due to bulk diffusion from the interior of the particles to the defects and then to the gas phase.

A different situation occurs for higher heating rates, where the endotherm due to diffusion along the defects has passed the endotherm due to bulk diffusion, the former now occurring at higher temperatures than the latter. Again, in order to achieve sufficient mass transport from the particle interior to the gas phase it is required that bulk diffusion as well as diffusion along the defects contribute. However, the N atoms that might be supplied by bulk diffusion in the middle of the particles cannot reach the gas phase via the diffusion along defects when applying high heating rates, because the latter process requires higher temperatures now. This means that the endotherm due to bulk diffusion remains relatively unimportant under these circumstances and may not be observed (it is generally only the high temperature endotherm that will be observed in two interdependent processes). In other words, the endotherm observed in DSC traces with high heating rates corresponds to the diffusion along defects. This range is indicated by T_d in Fig. 3.

Concluding, our DSC experiments on the outgassing of $R_2Fe_{17}N_x$ particles have shown that the outgassing depends on bulk diffusion as well as the diffusion along defects. For low heating rates, the outgassing rate is controlled by bulk diffusion whereas for high heating rates the outgassing rate is controlled by the diffusion along defects.

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