



Kinetic studies of hydrogen desorption in SmCo 2/17-type sintered magnets

M. Zakotnik*, D. Prospero, A.J. Williams

Department of Metallurgy and Materials, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK

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ABSTRACT

Hydrogen is used as a processing tool in the formation of powder from SmCo 2/17-type sintered magnets for recycling purposes. Fully dense 2/17-type sintered magnets (based on the composition $\text{Sm}(\text{Co}_{0.70}\text{Fe}_{0.21}\text{Cu}_{0.07}\text{Zr}_{0.02})_{7.49}$) were subjected to hydrogen decrepitation (HD) and the degassing behaviour of the resulting hydrogen solution was then studied by means of differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The hydrogen desorption is shown by DSC as an endothermic peak in the temperature range 433–473 K. The kinetics of degassing was investigated by measuring the mass losses using TGA. Understanding the degassing mechanism is of greater importance in the magnet recycling industry as the full recovery of the magnetic properties of $\text{Sm}_2\text{Co}_{17}$ -type sintered magnets is dependant on the amount of Hydrogen left in the powder after HD processing.

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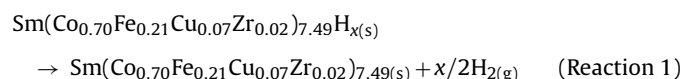
1. Introduction

Conventionally sintered rare earth permanent magnets are produced by powder metallurgy. The alloy is exposed to hydrogen causing hydrogen decrepitation (HD) of the alloy and the formation of a powder with $\sim 100 \mu\text{m}$ particle size. This is further milled to $\sim 5 \mu\text{m}$ particle size, resulting in single crystals. These crystals have a preferred direction of magnetisation, and thus can be aligned in a magnetic field and pressed to give a green compact that is sintered under vacuum at $\sim 1508 \text{ K}$ for 1 h followed by solution treatment.

Since, hydrogen has a high solubility and mobility (diffusivity) in many crystalline and amorphous alloys, it can cause significant changes in physicochemical and mechanical properties such as embrittlement. Hydrogen embrittlement of magnetic alloys has been the subject of intensive work, especially in the case of NdFeB and SmCo alloys and is now a well established technique to produce any sintered rare earth type magnets (see for example [1]). Previous work has shown that $\text{Nd}_2\text{Co}_{17}$ and $\text{Sm}_2\text{Co}_{17}$ compounds absorb hydrogen at moderate temperature and pressure to form a range of hydrogen solutions [2,3]. Earlier investigations utilising this system have shown solid solution/type behaviour [4]. In particular the effect of pressure and temperature on hydrogen uptake in $\text{Sm}_2\text{Co}_{17}$ alloys has been previously studied [5,6]. It was initially concluded that heating the alloy to 423 K was necessary in order

to achieve hydrogen absorption. However, later reports demonstrated that hydrogen absorption could reach saturation at 10-bar pressure at room temperature when left for 48 h [7]. Hydrogen absorption studies have been carried out on permanent magnetic alloys with the general formula, $\text{Sm}_2(\text{Co,Fe,Cu,Zr})_{17}$, however subsequent degassing behaviour has not been reported. Degassing of hydrogen from $\text{Sm}(\text{Co}_{0.70}\text{Fe}_{0.21}\text{Cu}_{0.07}\text{Zr}_{0.02})_{7.49}\text{H}_x$ in this work has been studied, using TG and DSC.

A common assumption employed in all the experiments is that the measured properties are related (directly) to the concentration of the product and/or reactant, and so the extent of reaction (α), and the rate of the specific chemical reaction ($d\alpha/dt$) is determined with time (isothermal) or temperature (dynamic). The overall degassing reaction can be expressed:



In this circumstance, it would be beneficial to employ a kinetic analysis that allows us to evaluate the role of activation energy as well as establishing whether the degassing process obeys single or multi-step kinetics. Both tasks can be accomplished by using iso-conversional methods that [8] have found numerous applications in kinetic analysis of thermally stimulated processes and of solid solution type systems. However, there appears to be no reports on the application of these methods to the thermal degassing of the hydrogen from the $\text{Sm}_2(\text{Co,Fe,Cu,Zr})_{17}$ based magnetic powder. By using $\text{Sm}_2(\text{Co,Fe,Cu,Zr})_{17}$ as a model system, the present paper initiates the novel application and demonstrates that isoconversional methods can provide new opportunities in exploring the kinetics in the

* Corresponding author. Tel.: +44 121 414 5165/3690; fax: +44 121 414 5247.
E-mail address: miha.zakotnik@gmail.com (M. Zakotnik).

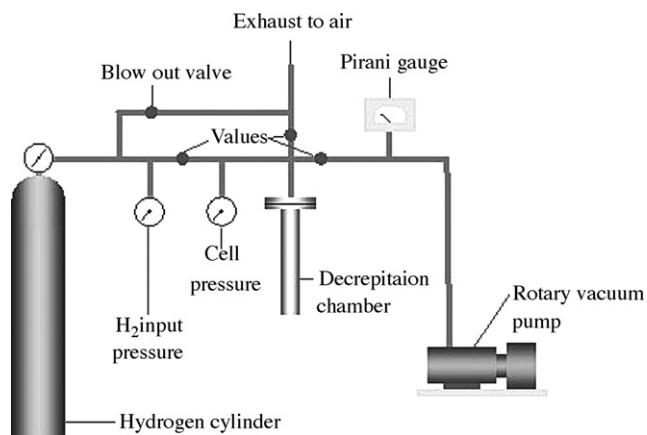


Fig. 1. Hydrogen rig.

$\text{Sm}_2(\text{Co,Fe,Cu,Zr})_{17}$ -type magnetic materials. The present study is aimed to better understand the degassing process of the HD treated magnets. Degassing process is a crucial stage in the process of recovering the magnetic properties and microstructural changes of the powders that can be used in turn to recycle sintered rare earth-type magnets.

2. Experimental procedures

The $\text{Sm}(\text{Co}_{0.70}\text{Fe}_{0.21}\text{Cu}_{0.07}\text{Zr}_{0.02})_{7.49}\text{H}_{x(s)}$ alloy (hereafter referred as 2/17) was prepared in our laboratory using the gaseous hydriding system, shown in Fig. 1. The procedure followed was to load sintered magnets based on 2/17 into the hydrogenation chamber, hydrogen was then admitted to the chamber at a pressure of 10 bar at room temperature. Completion of the reaction was determined when the pressure in the chamber stabilised, indicating that no more H_2 was being absorbed. The hydrogen content of hydrogenated samples was determined by weight measurement using an IGA (HIDEN Analytical Intelligent Gravimetric Analyser, with sensitivity $\pm 5 \mu\text{g}$) at pressures of up to 10 bar at room temperature. Simultaneous TG/DSC measurements were performed using a Netzsch model 404 instrument with a high temperature furnace, under a flow rate of argon at $100 \text{ cm}^3 \text{ min}^{-1}$. The set of samples consisted of $\sim 100 \text{ mg}$ contained in an alumina crucible and subjected to different heating rates of 1, 2, 5, 10, and 15 K min^{-1} from ambient temperature to about 673 K. A flow of argon was used with the TG and DSC in order to carry away the hydrogen after desorption and to prevent oxidation of the samples.

2.1. Kinetics for non-isothermal analysis

Experimental techniques used in solid-state kinetics generally cannot separate the reaction rates of the elementary steps and physical processes (diffusion, adsorption, desorption, nucleation, nuclei growth) involved in a reaction but instead can provide a measure for the overall rate of a process that usually involves several steps with different activation energies [9].

Despite these limitations, TG and DSC analysis are the most commonly used tools in order to perform kinetic studies. TG is indeed a convenient technique for studying the kinetics of processes involving gas–solid reactions, by following the weight changes of the samples with time [10].

In our study the weight loss occurring during the desorption of H_2 from 2/17 H_x solution makes this system suitable for thermogravimetry (TG) analysis. On the other hand, thermally stimulated degassing can be studied using the DSC by measuring the Enthalpy of the overall reaction.

Kinetic information can be extracted from both dynamic experiments using various methods.

The most general equation to describe the kinetics of this process is shown in the following equation:

$$\frac{d\alpha}{dt} = k(T, p)f(\alpha) \quad (1)$$

The fraction of decomposition $\alpha(t)$ is defined as

$$\alpha(t) = \frac{W_i - W_t}{W_i - W_f} \quad (0 \leq \alpha(t) \leq 1) \quad (2)$$

where W_t is the weight percent of the sample at any time t and W_i and W_f are the initial and final weight percents, respectively.

In the kinetic equation $k(T, p)$ is the rate constant generally dependent on pressure (p) and absolute temperature (T). The actual macroscopic reaction mechanism is represented as $f(\alpha)$, later in the paper called the *reaction model* [11–14].

In the operative range of temperature we can assume that pressure in the system is approximately constant, which allows k to be expressed by the Arrhenius equation (3) [15].

$$k(T) = Ae^{-E_a/RT} \quad (3)$$

where E_a is the activation energy, A the pre-exponential factor, R the gas constant and T is the temperature. The set of E_a , A and $f(\alpha)$ for each kinetic experiment is called the kinetic triplet, which fully define the kinetics of the process.

However E_a and A are strongly dependant on the chosen reaction model which is usually not known *a priori*, hence isoconversional methods, which are reaction model independent, are particularly suitable for this analysis [9]. The Friedmann method belongs to this category and can be used to extract the kinetic triplet from TG and DSC experiments respectively.

In the case of non-isothermal experiments we can make the trivial transformation where β is the heating rate (dT/dt):

$$\frac{d\alpha}{dT} = \frac{1}{\beta} \frac{d\alpha}{dt} \quad (4)$$

Combining Eqs. (1), (3) and (4) gives:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-E_a/RT} f(\alpha) \quad (5)$$

By taking logarithms, we obtain the Friedman equation:

$$\ln\left(\beta \frac{d\alpha}{dT}\right) = \ln A + \ln(f(\alpha)) - \frac{E_a}{RT} \quad (6)$$

From the TG experiment $\alpha(T)$ is measured and plotting $\ln(\beta(d\alpha/dT))$ against $1/T$ gives the activation energy and pre-exponential factor at fixed values of α and varying heating rates.

By plotting $f(\alpha)$ versus α we can finally get the reaction model [9].

To calculate the kinetic triplet from the DSC curve the Kissinger method is used (ASTM E698 [16]) whose utilisation relies on the following equation:

$$\ln\left(\frac{\beta}{T_{\max}^2}\right) = -\frac{E_a}{RT} + \text{const} \quad (7)$$

The activation energy can be calculated by plotting $\ln(\beta/T_{\max}^2)$ against $1/T_{\max}$ or where T_{\max} is the temperature corresponding to the maximum of $d\alpha/dT$. Empirical reaction order (n) was then extrapolated by measuring the degree of symmetry of the peak shape [17]. Knowing the reaction order, A was then computed by:

$$A = \frac{\beta E_a}{RT} \left[1 + (n-1) \frac{2RT_{\max}}{E_a}\right] e\left[-\frac{E_a}{RT_{\max}}\right] \quad (8)$$

The knowledge of reaction order, and therefore the assumption of “ n order” reaction model and the fact that T_{\max} values

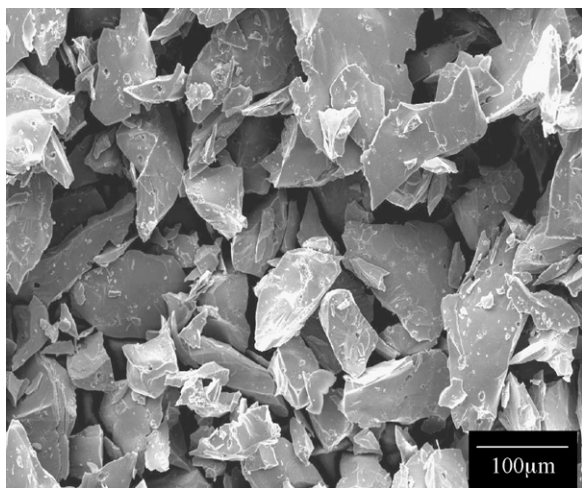


Fig. 2. Secondary SEM image of decrepitated 2:17 material after exposure to hydrogen at 10 bar pressure and at 298 K.

do not correspond to the same α at different heating rates [8] makes the method not strictly isoconversional. Therefore, in this paper the Kissinger method is used exclusively for comparison purposes.

3. Results and discussion

In the present work, hydrogen absorption has been achieved at room temperature and this differs from the earlier work which indicated that it was necessary to heat the alloys to around 423 K before hydrogen absorption could be obtained. It now appears that insufficient time for room temperature absorption was allowed in the earlier investigations. The powder obtained after room temperature exposure is shown in Fig. 2 and is flake-like in appearance indicating an “onion skin” type fracture process whereby thin layers are progressively removed from the magnet surface.

The pressure–composition IGA isotherm of 2/17 at 298 K measured on absorption in the IGA is shown in Fig. 3. The hydrogen uptake results in the formation of a range of hydrogen solutions, with a final composition of $\text{Sm}(\text{Co}_{0.70}\text{Fe}_{0.21}\text{Cu}_{0.07}\text{Zr}_{0.02})_{7.49}\text{H}_{1.4}$, at 10 bar, to ~ 0.25 wt% hydrogen. For longer hydrided times there was no further change of the hydrogen content. However for shorter times lower hydrogen content was observed.

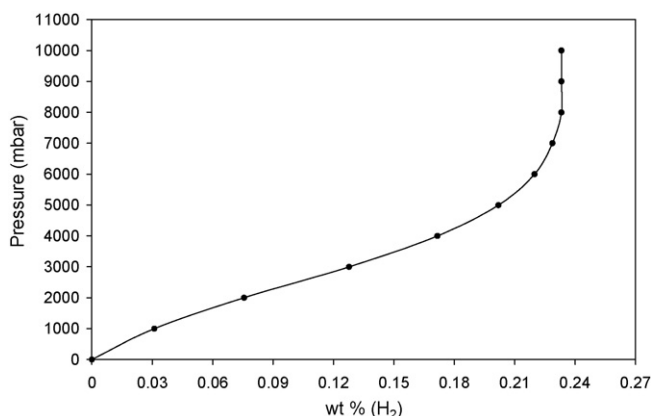


Fig. 3. Pressure dependence of weight change in the 298 K isotherm for the 2:17 alloy, evaluated by IGA.

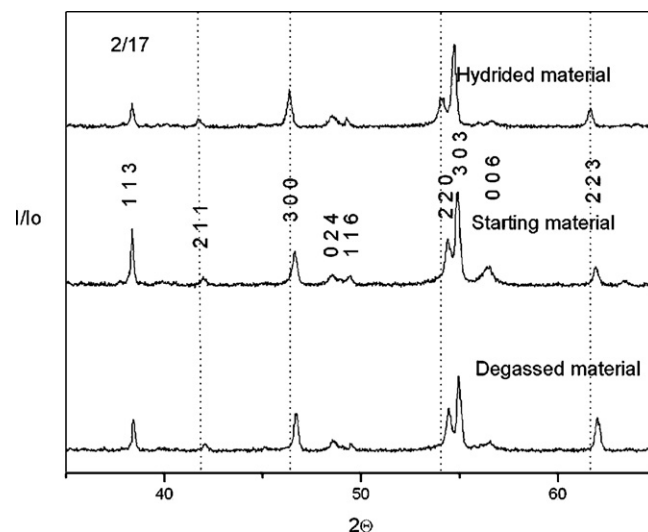


Fig. 4. XRD patterns of 2/17 at room temperature.

3.1. XRD analysis

Room temperature X-ray powder diffraction patterns for $\text{Sm}(\text{Co}_{0.70}\text{Fe}_{0.21}\text{Cu}_{0.07}\text{Zr}_{0.02})_{7.49}$, $\text{Sm}(\text{Co}_{0.70}\text{Fe}_{0.21}\text{Cu}_{0.07}\text{Zr}_{0.02})_{7.49}\text{H}_x$ and degassed $\text{Sm}(\text{Co}_{0.70}\text{Fe}_{0.21}\text{Cu}_{0.07}\text{Zr}_{0.02})_{7.49}$ at (200 °C) are shown in Fig. 4. The peaks of the hydrogenated $\text{Sm}(\text{Co}_{0.70}\text{Fe}_{0.21}\text{Cu}_{0.07}\text{Zr}_{0.02})_{7.49}\text{H}_x$ solution occur at slightly lower angles which indicate that the unit cell has expanded on hydrogen absorption without a change in the crystal structure. This result indicates that the unit cell volume of starting 2/17 and degassed 2/17 are the same, suggesting that lattice parameter and unit cell volume are successfully restored after degassing.

3.2. Thermogravimetric analysis data

Fig. 5 shows TG curves corresponding to dynamic experiments carried out at different heating rates: 1, 2, 5, 10 and 15 K min^{-1} . The average mass loss of the starting material was 0.16 ± 0.02 . This value is lower than that measured by IGA, which is most likely due to a greater degree of absorption reaction occurring in the IGA. Furthermore, the possible explanation for the discrepancies in the absorbed and desorbed hydrogen is due to the use of differ-

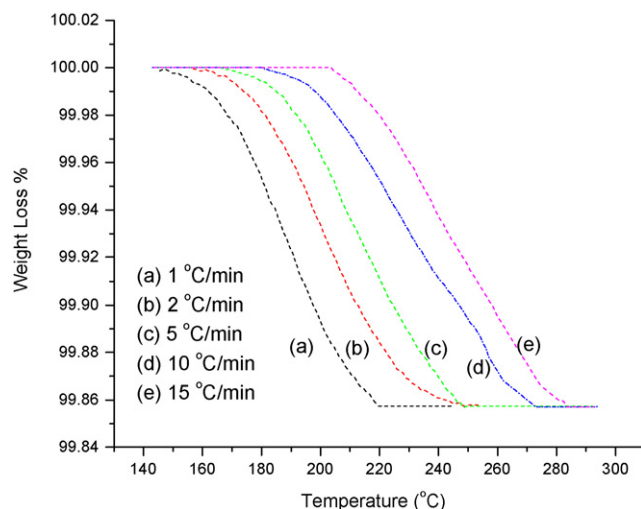


Fig. 5. Maximum loss according to formula $\text{Sm}(\text{Co}_{0.70}\text{Fe}_{0.21}\text{Cu}_{0.07}\text{Zr}_{0.02})_{7.49}\text{H}_x$ heated in Ar.

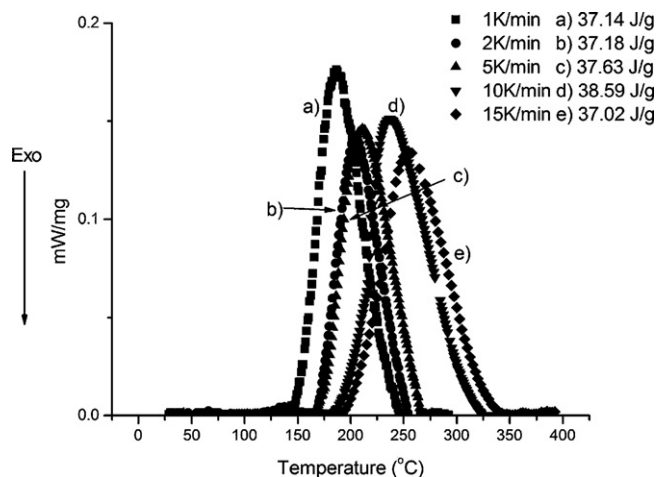


Fig. 6. Normalised DSC curves for the thermal degassing of $\text{Sm}(\text{Co}_{0.69}\text{Fe}_{0.21}\text{Cu}_{0.068}\text{Zr}_{0.019})_{7.49}\text{H}_x$ heated in Ar.

ent equipment in the two processes. However, from XRD analysis it is shown that no hydrogen is present in the powder after degassing.

3.3. DSC analysis

The amplitude of the DSC peak increases with increasing heating rate which is shown in Fig. 6. The average enthalpy of formation for the degassing of $\text{Sm}(\text{Co}_{0.70}\text{Fe}_{0.21}\text{Cu}_{0.07}\text{Zr}_{0.02})_{7.49}\text{H}_{1.4}$ solution was $37.51 \text{ J g}^{-1} \pm 0.65$ for all the heating rates.

3.4. Reaction order

The reaction mechanism by the Friedman method for $0.2 \leq \alpha \leq 0.8$ was determined using Eqs. (5) and (6), and was found to be a first order mechanism [9], which is shown in Fig. 7, hence there is a linear relationship for all the heating rates.

Reaction order in the Kissinger method is extracted by graphical analysis of the DSC peak shape [17]. Table 1 shows the computed empirical values of the reaction order at different heating rates. The mean value is 1.01 ± 0.08 . This means that, according to the Friedman method, the reaction is a first order.

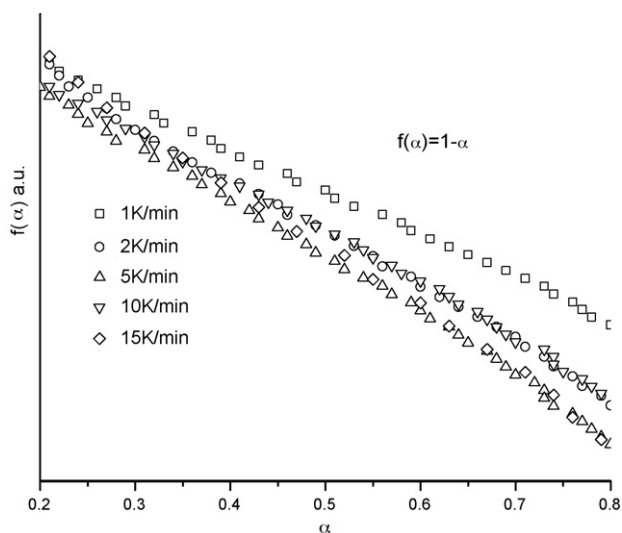


Fig. 7. Determination of the reaction mechanism for degassing of the $\text{Sm}(\text{Co}_{0.70}\text{Fe}_{0.21}\text{Cu}_{0.07}\text{Zr}_{0.02})_{7.49}\text{H}_x$ solution at different heating rates.

Table 1

Kinetic results of reaction order (n) for different heating rates (by Kissinger method).

Heating rate (K min^{-1})	$n (\pm 0.08)$
1	1.01
2	1.03
5	0.98
10	0.90
15	1.11

3.5. Activation energy and pre-exponential factor

Calculation of the activation energies for the degassing process of the $\text{Sm}(\text{Co}_{0.70}\text{Fe}_{0.21}\text{Cu}_{0.07}\text{Zr}_{0.02})_{7.49}\text{H}_{1.4}$ solution at which 50% of hydrogen was degassed resulted in around 99.5 kJ mol^{-1} and 100 kJ mol^{-1} , using Friedman and Kissinger methods respectively. The Friedman analysis allowed us to make the following conclusions: the E_a dependence was evaluated for the complete conversion rate of desorption and the results are presented in Fig. 8. The overall degassing value ($0.05 \leq \alpha \leq 0.96$) for the activation energy was averaged and the result was around 100 kJ mol^{-1} , ± 10 .

Because averaging can only be applied to randomly varying values, averaging of systematic dependency of E_a on α is statistically meaningless. However in our case the change in E_a is several percent of the mean value, which allow us to take the average value as representative for the whole process [9]. Fig. 8 indicates that the conversion dependence of the effective activation energy has a slight descending shape, which might lead to the conclusion that the process is complicated by diffusion, however when the errors are taken into account the variation of E_a versus α is constant. The initial stage of desorption ($\alpha < 0.2$) shows a higher activation energy of around $123 \text{ kJ mol}^{-1} \pm 10$. The latter stage ($\alpha > 0.8$) shows a decrease in the activation energy to around $84 \text{ kJ mol}^{-1} \pm 10$. Values of the activation energy and the pre-exponential factor at 50% conversion correspond to $100 \text{ kJ mol}^{-1} \pm 10$ and 18 s^{-1} respectively.

The identified reaction order, obtained from the peak shape using the Kissinger analysis, allowed the pre-exponential factor to be determined:

$$A = \frac{\beta E_a}{RT_{\max}^2} e\left(\frac{E_a}{RT_{\max}}\right) \quad (9)$$

The overall values for both methods are summarised in Table 1.

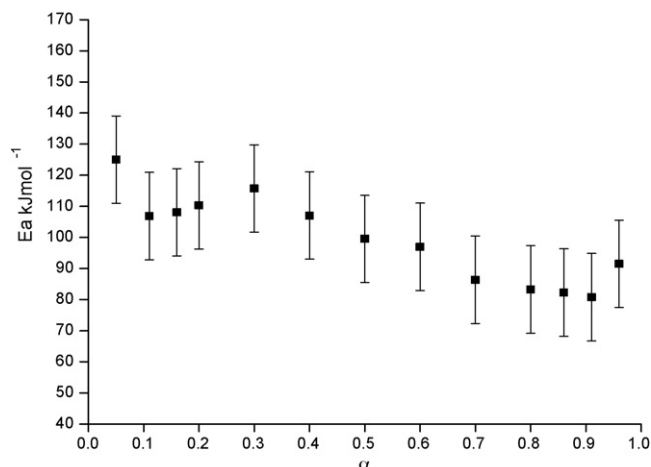


Fig. 8. Dependencies of E_a on α for degassing of $\text{Sm}(\text{Co}_{0.70}\text{Fe}_{0.21}\text{Cu}_{0.07}\text{Zr}_{0.02})_{7.49}\text{H}_x$ solution.

4. Conclusions

A $\text{Sm}(\text{Co}_{0.70}\text{Fe}_{0.21}\text{Cu}_{0.07}\text{Zr}_{0.02})_{7.49}\text{H}_{1.4}$ solution was formed at room temperature using a constant pressure of hydrogen at 10 bar. The degassing of the solution was studied by thermogravimetric analysis (TGA) and by differential scanning calorimetry (DSC) at different heating rates between 1 and 15 K min^{-1} , in an argon flow. The powder had to be heated to elevated temperatures in order that the hydrogen would be removed from the 2/17-type sintered powder. During degassing by using the TG and DSC within the conversion range ($0.2 \leq \alpha \leq 0.8$) a single reaction takes place (solid \rightarrow solid + gas), as suggested in [Reaction 1](#). Furthermore the fact that the whole process was pressure independent allowed us to conclude that the E_a dependence for the degassing is likely to represent the overall reaction kinetics of a single step reaction process, which gives us a first order mechanism reaction confirmed by an empirical reaction order equal to 1 using the Kissinger method. XRD analysis shows that the process is reversible. The constant behaviour of $E\alpha$ vs α throughout the whole degassing process suggests that diffusion plays almost no role in the reaction, although further investigation is required to confirm this. In conclusion, the above approach has yielded important insights into the reaction mechanism of degassing of 2/17 magnets. A general understanding of the degassing process may prove fundamental in order to facilitate full recovery of the magnetic properties of other rare earth magnetic alloys.

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