Thermochimica Acta 474 (2008) 36–40

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Application of a thermogravimetric technique for the determination of low nitrogen solubilities in metals: Using iron as an example

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ARTICLE INFO

Article history:
Received 26 February 2008
Received in revised form 7 May 2008
Accepted 13 May 2008
Available online 18 May 2008

Keywords:
Thermogravimetric technique
Nitrogen solubility
Gas–metal interaction

ABSTRACT

A thermogravimetric technique was explored in order to precisely investigate the low nitrogen solubilities in metals. The thermogravimetry (TG) set-up is presented in detail. By the optimization of the set-up, a good baseline (noise level <2 μg, curve drift: ±1–4 μg/h) was obtained. The measurements of nitrogen solubility in iron are described. The weight signal arising from the nitrogen dissolved in iron was recorded continuously as a function of time under various experimental conditions. The nitrogen solubility can be calculated from the weight change between the beginning of nitrogen introduction and the steady state (equilibrium). There is a good agreement between the present measurements and the data in the literature determined by alternative methods such as chemical analyses of quenched samples, Sieverts' method as well as thermogravimetric technique. In addition, a so-called isothermal stepping TG process shows that the TG set-up has a sufficient sensitivity to display the effect of the phase transformation of iron from body-centered cubic phase to face-centered cubic phase on the nitrogen solubility.

1. Introduction

Gas–metal interactions are of great interest, both from a technological and a scientific point of view. Such interactions can result in the dissolution of non-metal atoms like N, H and O, etc. which has a big influence on the properties of metals [1–5]. In past years, two major methods, the Sieverts' method and the quenching method, were explored to investigate the kinetics of the dissolution of nitrogen in pure metals or alloys [6]. The former method was used by Sieverts in the 1900s to measure the solubilities of gases, primarily nitrogen in liquid metals and their alloys. A metallic sample, contained in a reaction vessel, is equilibrated with a given volume of gas at a certain temperature. The amount of gas dissolved in the sample is measured as a pressure change by a manometer. The gas solubility is determined by calculating the volume of gas absorbed. However, the drawback of Sieverts' method is the difficulty of obtaining an accurate volume of the reaction vessel at high temperature. Additionally, this technique involves the risk of evaporation of metal that condenses on the wall of the reaction chamber. The nitrogen may react with these deposits or it can be adsorbed. The impact of these effects becomes greater at higher temperature [7].

The solubility of nitrogen in a metal can also be determined by the quenching method, where the metal is held in contact with the gas until equilibrium is reached. Then it is rapidly cooled in a quenching medium. After this the amount of nitrogen in the metal is determined by chemical analysis. In this technique, the loss of nitrogen during the cooling and solidification leads to a lower value of the nitrogen content compared to the real value [7].

There are only a few reports about the use of the thermogravimetric technique to measure the gas solubility in metals. It was first used by Bale and Toguri [8] for determining the thermodynamic properties of sulfur in Cu–Fe under a mixture of H_2S and H_2. The weight change of the sample was recorded continuously under different chemical potentials of sulfur, which was adjusted by changing the volume ratios of H_2S/H_2. Recently, Bouchard and Kirkaldy [9] explored a modified thermogravimetric instrument to measure the nitrogen solubility in pure Fe and pure Ni metals under a mixture of N_2 and H_2 or N_2, H_2 and He. The experimental set-up is similar to the one used by Bale and Toguri [8], where a top-loading design is used. The inlet and outlet lines of gases are arranged in such a way that the gases flow across the sample upwards. The experimental results show that the thermogravimetric technique provides a high resolution. For example, a solubility as low as 0.00016 wt.% (1.6 ppm) at $P_{N_2} = 0.22$ bar in nickel was measured with this technique [9]. The advantage of this method is the *in situ* measurement, compared to *ex situ* techniques like the quenching method. Despite of the advantages, the TG method was not so often used in the past, and its methodical optimization like baseline calibration, purification of gases, etc. were not described

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doi:10.1016/j.tca.2008.05.005

in the literature. This will be demonstrated in this work taking the system nitrogen and iron as an example.

Generally, the nitrogen solubility in metals is very low. For example, the nitrogen solubility in α-Fe is about 3×10^{-3} wt.% at 900 °C and $P_{N_2} = 1$ bar [10]. Although a very high sensitivity (i.e. 0.1 μg) of the thermobalance is usually claimed by the manufacturers, it is necessary to optimize the TG set-up, in order to obtain highly accurate measurements, and to achieve the highest possible resolution. This procedure includes the improvement of the baseline reproducibility, long-time stability and resolution of the set-up.

In this study, the calibration of the baseline and optimization of the thermogravimetry (TG) set-up are introduced in detail. The feasibility of the TG method used to measure the nitrogen solubility in metals in general is proved, using iron as a reference material.

2. Experimental set-up and procedure

The measurements were carried out using a Netzsch Thermal Analyzer STA 449C *Jupiter*® equipped with a TG-sample carrier for large sample quantities as shown in Fig. 1, and described in detail in Ref. [11]. Samples weighing up to 5 g can be used. Ultrahigh purity gases (99.9999% for Ar and H_2, 99.999% for N_2, supplied by Linde AG) are used throughout the experiments. The flow rate of each gas is controlled by a mass-flow controller (MFC; Bronkhorst High-Tech B.V.). Before the gases are introduced into the reaction tube, they are additionally passed through a gas purifier (MicroTorr) to remove impurities (O_2, H_2O, CO and CO_2) to less than 1 ppb. Two pressure buffers are connected downstream from the TG to dampen the backside pressure fluctuations from the surrounding and the exhaust gas cleaning system. One of the pressure buffers is provided by NETZSCH Gerätebau GmbH. The second pressure buffer is self-made, which consists of a glass tube filled with glass fiber.

Some pieces of small plate-like sapphire crystals were used for the baseline calibration. The iron sample (Johnson Matthey) has a cylindrical shape (1 cm long and 1 mm in diameter) with a purity of 99.995%. The oxide layer of the iron sample was removed by sanding on a fine 3 M Scotch–Brite pad and subsequent etching in HCl (50%) for 30 min. Then the specimens were washed by distilled water and dried in flowing N_2. Subsequently the specimen was introduced in the alumina crucible (3.4 ml). The experimental procedure was carried out according to Fig. 2. The TG chamber is evacuated to 10^{-6} mbar and the sample is annealed for several hours under vacuum at 500 °C (step 1). This step is necessary because commercially available metals contain a certain amount of gases [12]. By this step the gas in the iron sample can be extracted into the vacuum. After this step (1), Ar is introduced while the furnace is heated to the reaction temperature (2). When the pressure of the furnace chamber reaches the ambient pressure (3), H_2 is added to the atmosphere in order to deoxidize the metal sample. After the sample is held in the mixture of Ar and H_2 for several hours (4), the N_2 is introduced (5). During step 5, the weight gain is continuously monitored by a computer until no further weight change is observed. Finally, the flow of H_2 and N_2 are stopped, and the furnace is switched off. The samples are cooled to room temperature under Ar atmosphere (6).

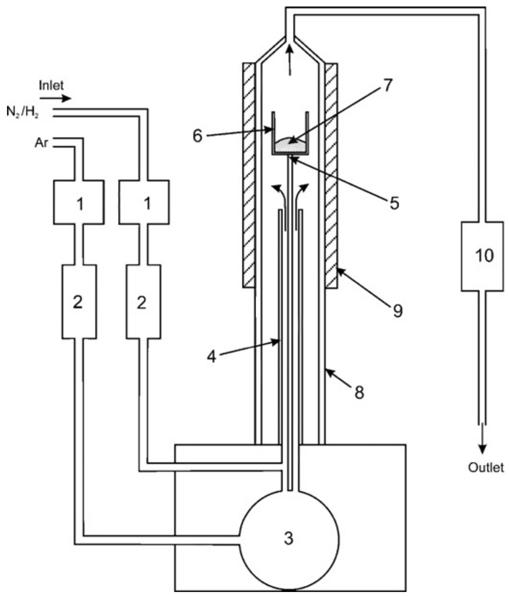

Fig. 1. Schematic diagram of the thermogravimetric apparatus: (1) mass flow controller, (2) gas purifier, (3) electrobalance, (4) alumina tube, (5) thermocouple, (6) crucible, (7) sample, (8) furnace, (9) heater, and (10) pressure buffer.

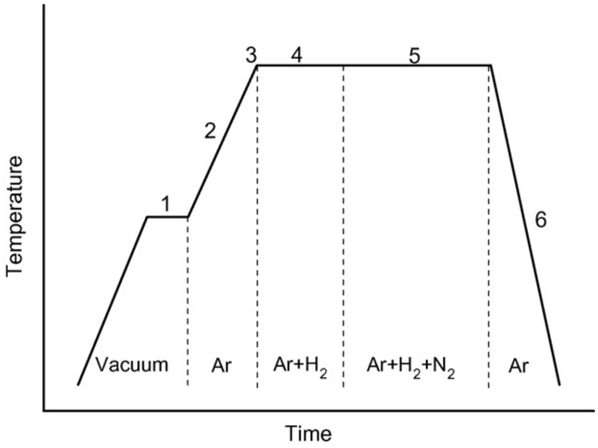

Fig. 2. Schematic illustration of temperature as a function of time for a TG measurement.

3. Results and discussion

3.1. Baseline calibration and optimization of the set-up

The plot of the weight signal *vs.* time for a TG system should be a straight line without any slope, called baseline, if an empty crucible, constant temperature and gas flow rate are used. But in a real TG experiment, the baseline is normally not a straight line: any perturbations of gases and temperature are causing deviations from a straight baseline, because the sample is subjected to the buoyancy exerted by the gases. This results in changes of the weight signal as the experimental conditions are varying. The force F caused by buoyancy on a sample is expressed by Archimedes' principle

$$F = \rho g V \tag{1}$$

where ρ is the density of the gas, g is the acceleration due to gravity and V is the volume of the sample. g and V remain constant during the experiment, but the buoyancy is depending on the density ρ of the gas. ρ depends on several factors like temperature, pressure, flow rate and composition of the gas. These influences must be minimized in order to have conditions which provide a constant baseline. Such a procedure is shown in Fig. 3 in correlation with Table 1 where the various experimental measures are compiled. Fig. 3 shows baseline measurements made under a constant temperature and gas flow rate using a sapphire sample. Different experimental conditions for curves (a_1)–(d) are given in Table 1. Gas pressure variations during the measurements can be reduced by improving ambient conditions. Another possibility is to install two pressure buffers downstream from the TG set-up as shown in

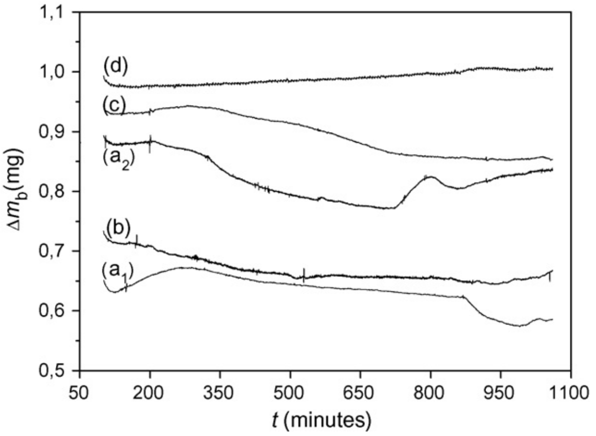

Fig. 3. Plots of the weight change (Δm_b) *vs.* time (t) using sapphire crystals as a sample under the constant flow rates of Ar and N_2 at 800 °C. Curves (a_1)–(d) correspond to different experimental conditions given in Table 1.

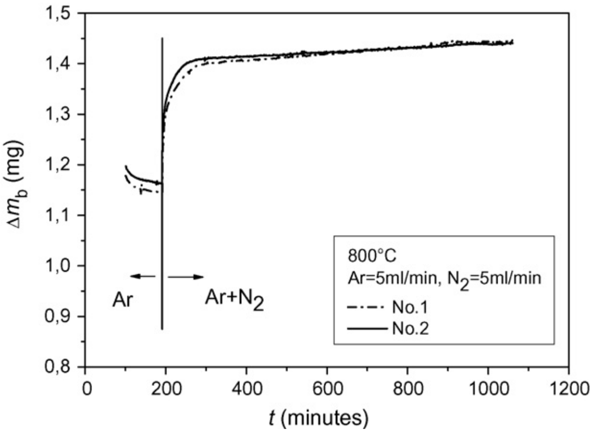

Fig. 4. Plots of weight change (Δm_b) *vs.* time (t) using a sapphire sample in two experimental runs (Nos. 1 and 2) under the same optimized set-up as used for the curve (d) in Fig. 3 and Table 1.

Fig. 1. Moreover, the gas flow rate has to be controlled by a MFC because a rotameter is not sufficient.

In Fig. 3, two curves (a_1) and (a_2) show the initial results under non-optimized conditions with backside pressure influences. The curve (a_1) shows a drastic drop of the weight signal at about 860 min arising from a sudden change of the ambient pressure. Since the gas is normally exhausted directly to the surrounding room atmosphere, the ambient pressure strongly affects the gas density and buoyancy in the reaction chamber. By keeping the pressure of the surrounding atmosphere as constant as possible (e.g., putting the gas outlet in a closed and static atmosphere), the curve drift becomes smaller (curve (b)). In addition, the pressure buffers are also helpful to alleviate the influence of the atmospheric pressure from the backside of the set-up. Compared to the curve (a_1) and (a_2), no sudden change in weight appears in curve (c) and also the long-term drift of curve (c) becomes smaller by the aid of the pressure buffers.

Besides the gas flow rate has to be controlled precisely to reduce measurement artifacts. To keep the gas flow rate as constant as possible, a MFC is a better choice compared to a rotameter. This is demonstrated by curve (d) in Fig. 3 where all described means of set-up optimization were applied.

If a constant baseline value is achieved under the same experimental conditions required for the iron experiments, a corrected weight change (Δm) of the sample is obtained by

$$\Delta m = \Delta m_\mathrm{m} - \Delta m_\mathrm{b} - \mathrm{offset} \qquad (2)$$

where Δm_m is the measured weight change from TG experiments, Δm_b is the weight change from the measurement of the baseline, and the offset is used to set $\Delta m = 0$ at the beginning of the process investigated. If the experimental condition is changed, a new baseline measurement has to be carried out under the new experimental conditions.

For reliable experiments, the measurements not only have to be free from artifacts but must also be reproducible. This was tested by experiments shown in Fig. 4. The two curves were obtained under the same experimental conditions and processes. Only Ar is used at the beginning followed by the introduction of N_2. A sudden change of weight arises from the introduction of N_2. The two reproducible curves indicate that the corrected weight change of a sample according to Eq. (2) is reliable if a baseline check is carried out under the same experimental conditions as the following measurement for a sample, and the experimental set-up is optimized to high resolution. The best is, however, to measure the baseline and the sample several times in order to ensure that reproducibility is given. Especially if experimental conditions like e.g. gas type or flow rate were changed. The two curves in Fig. 4 are given exemplarily, more curves would superpose the ones shown. Because the measurements are long-term experiments (several 20–100 h), the drift of the system reps. drift of the weight signal with time must be as small as possible and the signal to noise ratio best. The lowest noise level and curve drift obtained from many measurements are ±1–2 μg and ±1–4 μg/h, respectively. These values are better than the technical specification given by the instrument producer.

Table 1
Experimental conditions for curves (a_1)–(d) in Fig. 3

Curve	Adjusting ambient conditions	Pressure buffer	Gas flow rate controller	
			Rotameter	MFC
a_1			×	
a_2			×	
b	×		×	
c		×	×	
d	×	×		×

3.2. Measurements of nitrogen solubility in solid iron

The measurements of nitrogen solubility in metals were carried out under constant experimental conditions, i.e., constant temperature and gas flow rate. The optimization of the set-up for the measurements of nitrogen solubility in solid iron was carried out according to the procedure described in Section 3.1. Fig. 5 shows typical plots of the weight change *vs.* reaction time using iron metal and sapphire as the samples. Curve (1) is a baseline obtained using the sapphire crystals as a reference sample. Curve (2) is the measured curve for the iron sample. These two curves were measured under the same experimental conditions. The corrected weight change of iron (curve (3)) is obtained according to Eq. (2). After N_2 is introduced, curve (3) shows a weight increase ($1210\ \mathrm{min} \le t \le 1950\ \mathrm{min}$) followed by a plateau ($t \ge 1950\ \mathrm{min}$). This can be interpreted as the establishment of a gas–metal equilibrium. The weight gain is attributed to the solution of N in Fe. The nitrogen solubility can then be calculated from the weight change (Δm^* in Fig. 5) between the beginning of nitrogen introduction and the equilibrium state.

The solubility of nitrogen (X_N) in Fe in equilibrium with a partial pressure of nitrogen (P_{N_2}) is calculated as follows:

$$X_\mathrm{N} = \frac{n_\mathrm{N}}{n_\mathrm{Fe} + n_\mathrm{N}} \qquad (3)$$

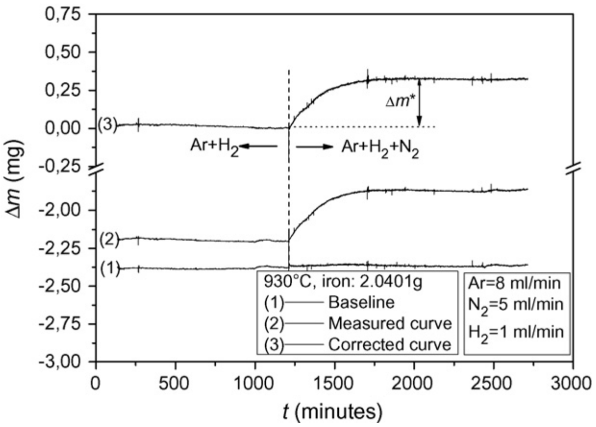

Fig. 5. Weight change (Δm) as a function of time (t) for two samples at a temperature of 930 °C. Curve (1) is the baseline obtained using a sapphire crystal as a reference sample. Curve (2) is the measured curve for the iron sample. The corrected weight change of iron (curve (3)) is obtained according to Eq. (2).

where X_N is the mole fraction of nitrogen in Fe, n_N and n_{Fe} are the moles of N and Fe, respectively. The value of n_N can be calculated from the weight change (Δm^*) in Fig. 5. If N_2 is assumed to be an ideal gas, and the nitrogen solubility in metals is very low, then Sieverts' law is obeyed [13]. It states that the solubility of atomic N is proportional to the square root of the pressure of N_2,

$$X_N = KP_{N_2}^{1/2} \tag{4}$$

where K is the equilibrium constant for nitrogen dissolution, and P_{N_2} is the partial pressure of nitrogen gas. Application of the Van't Hoff's equation gives the variation with temperature of the equilibrium constant at constant pressure and hence also of the corresponding equilibrium solute concentration:

$$\frac{\mathrm{d}\ln K}{\mathrm{d}(1/T)} = \frac{-\Delta H^\circ}{R} \tag{5}$$

where ΔH° is the standard enthalpy of solution of the gas, T is the absolute temperature, and R is the universal gas constant.

This equilibrium constant K obtained from our TG measurements at various temperatures T is plotted in Fig. 6 together with data from various other measurements. There is a good agreement between the results of the present and previous studies. A large solubility increase is observed at 915 ± 15 °C. For pure iron, the temperature of the phase transformation from body-centered cubic (bcc) phase to face-centered cubic (fcc) phase is 912 °C at 1 bar [9]. The change of nitrogen solubility in Fe at 915 ± 15 °C arises from the different solubility in these two phases.

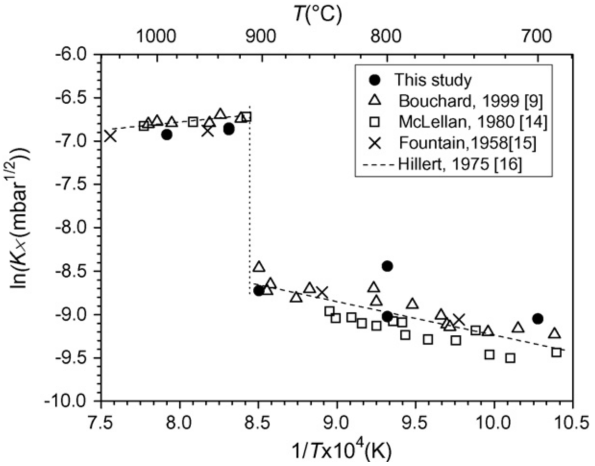

Fig. 6. Plots of the equilibrium constant (K) for nitrogen dissolution in iron *vs.* reciprocal temperature ($1/T$). Results from Refs. [9,14,15] were obtained by thermogravimetric method, quenching methods and Sieverts' method, respectively. The dashed line is calculated from the expression given by Hillert and Jarl [16].

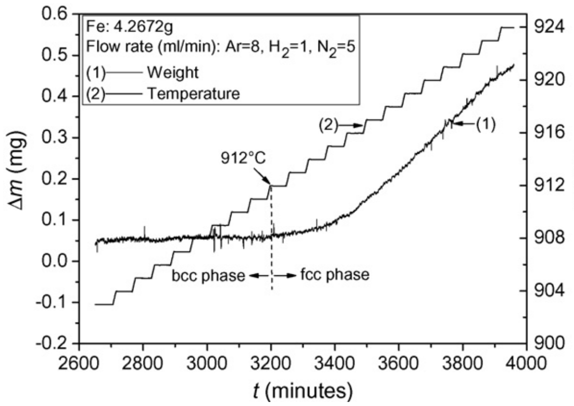

Fig. 7. Plots of the corrected weight change (Δm) (left) and temperature (T) (right) *vs.* time during an isothermal TG stepping process.

Such an effect of a phase transition can be determined in more detail by the so-called isothermal stepping TG process. As shown in Fig. 7, the temperature is controlled as a "step" profile. This profile was generated by (I) a constant heating rate of 0.1 °C/min for 9 min, followed by (II) holding the temperature for 50 min. This procedure was repeated for several times. Before this process, the iron sample was held at 903 °C under the mixture of Ar, H_2 and N_2 for 25 h, in order to achieve the gas–metal equilibrium. No apparent weight gain is observed when the temperature increases from 903 to 912 ± 1 °C because the change of solubility in this temperature range is very small. Starting from 912 ± 1 °C, the weight increases because the phase transformation from bcc phase to fcc phase occurs. This process shows a sufficient sensitivity of the thermobalance to display the phase transformation.

The thermogravimetric technique has proven suitable to measure low nitrogen solubility in metals, e.g. 1.6×10^{-2} wt.% in Fig. 6. But when the solubility is below 1×10^{-3} wt.%, large errors could arise due to the resolution of the limit of thermobalance for the given set-up.

There are also several potential sources of errors for the measurements. Such a technique is not suitable for the gas–metal couples that lead to the formation of nitrides or hydrides. In that case, the measurements of the weight gain will not reflect the actual amount of gas dissolved interstitially in the metals. Impurities in the iron sample like V [15] and Si [17] could in principle react with nitrogen to form nitrides. However, the concentrations of these impurities in iron used in the present study are very low (for example: V/0.06 ppm; Si/8.3 ppm). If these impurities could be transformed to nitrides, it would result in a weight change of about 5×10^{-4} wt.%, which is below the detection limit (1×10^{-3} wt.%) of the TG set-up. Moreover, the reaction rate of Si and N_2 is very low at temperature below 1350 °C [17,18]. Therefore, it is assumed that these impurities cannot result in a large error in the present measurements. The measurements were carried out in the atmosphere containing hydrogen as shown in steps (4) and (5) of Fig. 2. Hydrogen is also soluble in Fe. An equilibrium between the metal and the surrounding H_2 is reached in step (4), so that no further hydrogen pickup occurs during step (5). Another possible source of errors in solubility measurements is the determination of the point where the gas–metal equilibrium is achieved. For future work, experiments with the combination of absorption and desorption of nitrogen in the metal could give additional information about the kinetics of the dissolution process by observing the transient until the establishment of the gas–metal equilibrium.

4. Summary

As an *in situ* technique, the thermogravimetry provides a simple and efficient method to record the mass change with time or temperature. A high performance of the TG set-up was attained by optimizations of the baseline reproducibility, long-time stability and resolution of the instrument. This technique can be used to detect a very low weight change (1×10^{-3} wt.%). These advantages were further demonstrated in the measurement of the solubility of nitrogen in gallium [19], and the study of the reaction kinetic of gallium under flowing ammonia [11]. All these results illustrate the reliability of the TG technique for the investigation of the gas–metal interactions.

Acknowledgements

We thank Rainer Apelt for his technical assistance. This project is financially supported by the German Ministry of Education and Science BMBF under Contract 01BM158.

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