Journal of Thermal Analysis, Vol. 30 (1985) 121–128

HIGH-TEMPERATURE THERMOGRAVIMETRIC ANALYSIS. INFLUENCE OF GAS PRESSURE ON KINETICS OF REACTIONS IN THE SOLID STATE

G. Thomas and *F. Ropital*

DEPARTEMENT DE CHIMIE PHYSIQUE DES PROCESSUS INDUSTRIELS,
ECOLE NATIONALE SUPERIEURE DES MINES, 158 COURS FAURIEL,
42023 SAINT-ETIENNE CEDEX, FRANCE

A magnetic balance apparatus has been set up to follow reactions in the solid state under controlled conditions of pressure and temperature (25–1000°). Magnetic properties are characteristic of solid structures, and thermomagnetic analysis (T. M. A.) can give the variations of the sample susceptibility during the course of a reaction (susceptibilities of the new phases and of initial compounds not yet transformed). By continuous measurement of this susceptibility with the Faraday method, the conversion degree of the synthesis can be obtained.

T. M. A. has been used to study the influence of a gas on a solid–solid reaction in which no gas can be evolved or consumed. An example is given for iron tungstate synthesis: $Fe_2O_{3(s)} + WO_{3(s)} \rightarrow Fe_2WO_{6(s)}$. At 800° the reaction kinetics depends on the nature and the pressure of the gas.

In order to study solid–solid reaction kinetics, methods such as thermogravimetry are used when the emanation occurs, or more generally X-ray powder diffraction analysis, chemical analysis and other methods based on some physical property of the sample. Dilatometry and magnetic analysis are good examples of the latter. Studies on nickel ferrite [1–4], nickel molybdate [5] or cobalt tungstate [6] synthesis have been followed discontinuously at 25° and continuously at low temperature ($T < 500°$) with the magnetic method.

As solid-state reactions need higher temperature, we have developed a thermomagnetic analysis (T. M. A.) apparatus to measure magnetic susceptibilities up to 1000°. From these measurements the conversion degree of a reaction can be deduced. As the magnetic properties of a solid are characteristic of its structure, T. M. A. can give the rate of formation of the new phases. The basis of this method is presented, and the experimental study of iron tungstate synthesis is taken as an application of T. M. A.

The thermomagnetic method

a. Principle

To measure magnetic susceptibilities, the Faraday method [7], based on the force acting upon a sample in an inhomogeneous magnetic field, is used:

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

$$F = \text{grad}\,(\eta H)$$

where H is the applied magnetic field and η the magnetic moment.

For a given sample of mass m and mass susceptibility χ, the magnetic moment is $\eta = m\chi H$ and the magnetic force is

$$F = m\chi H \frac{\partial H}{\partial x}$$

With specially shaped polar pieces, a volume in which the product $H(\partial H/\partial x)$ is constant can be obtained [8]. In this part, the mass susceptibility is a linear function of the magnetic force. Such forces can easily be detected by means of a balance.

b. Magnetic balance apparatus

In our assembly, a Setaram MTB 10.8 microbalance is used. Its sensitivity is 10^{-7} Newton.

A Drusch EAF 11U electromagnet can produce a field up to $6.57 \cdot 10^5$ A m^{-1} and a product $H(\partial H/\partial x)$ up to $5.29 \cdot 10^{12}$ A^2 m^{-3}. The volume in which $H(\partial H/\partial x)$ is constant is $1.4 \times 1.4 \times 1.4 \cdot 10^{-6}$ m^3.

The sample can be heated in a Setaram HT 40 microfurnace up to 1000°. A vacuum and gas introduction system is connected to the balance.

The sample is placed in a gold vessel and the magnetic force due to the container and the atmosphere is subtracted from the experimental force to calculate the real mass susceptibility.

c. Thermomagnetic analysis feasibilities

Two purposes can be distinguished in the use of T. M. A.

T. M. A. can characterize the thermomagnetic behaviour of a solid, such as its susceptibility and transition points (Fig. 1, part A). The temperatures of such transformations can be detected by measuring the magnetic susceptibility versus temperature: T. M. A. signals will present unexpected variations when significant magnetic changes occur in the sample.

On the other hand, under isothermal conditions, the magnetic method is a useful tool to follow reaction kinetics (Fig. 1, part B). From the χ vs. time graphs and by using susceptibility addition laws, the conversion degree λ of the reaction can be deduced [9].

For solid–solid reactions without gas emanation, such as

$$\nu_A A_{(s)} + \nu_B B_{(s)} \rightarrow \nu_C C_{(s)}$$

$$\lambda(t) = \frac{\chi_{(t)} - \chi_0}{\chi_\infty - \chi_0}$$

where χ_0 is the initial mixture susceptibility and χ_∞ is the sample susceptibility when the reaction is over.

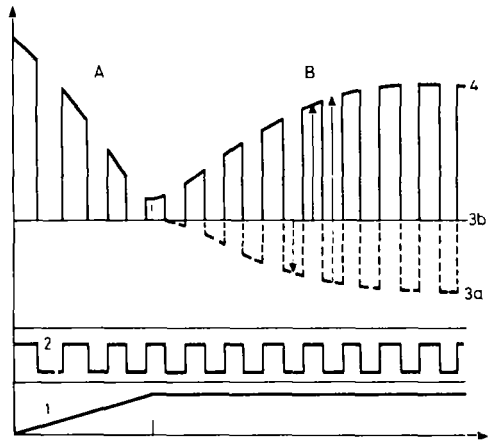

Fig. 1 Measurement sequences. 1. Temperature programming, 2. magnetic field programming, 3. mass variation signal (a) with and (b) without gas emanation, 4. magnetic force signal

This conversion degree can be calculated directly from the magnetic force measurement (Fig. 1) by a data acquisition device, if the final susceptibility is known. From time to time the magnetic field is not applied, to control the balance base-line.

d. Advantages and limits of the magnetic method

The first and principal limit of this method is that it can be applied only to reactions between products presenting sufficient susceptibility variations (χ_∞ quite different from χ_0) at the reaction temperature. However, the very high sensitivity of the balance permits the study of reactions such as nickel tungstate synthesis, with low $\Delta\chi$ (Table 1).

The sensitivity of the magnetic method decreases as the temperature rises (at high temperature, $T > 600°$, most compounds are paramagnetic and their susceptibilities follow the Curie–Weiss laws). Some reactions can not be studied continuously, and a quench is required to measure the sample composition at 25°.

In the magnetic method, the applied magnetic field can influence the synthesis kinetics. Some authors have noticed such effects on the reduction of oxides [10–12]. This point must therefore be clarified before the experimental results given by T. M. A. are analyzed.

A great advantage of this method is its good sensitivity, which is much higher than that of the Gouy method for instance. For the three synthesis mentioned in Table 1, the precision of the conversion degree was about 4%. Furthermore, small quantities of mixture are required (about $50 \cdot 10^{-6}$ kg). The temperature homogeneity in the sample is correct (heating by radiance), so the reaction conversion is the same in every part of the reacting species. This method gives access to the sample *global* composition.

Table 1 Magnetic susceptibility data on some solid–solid reactions followed by T. M. A.

Reaction	T, °C	$(\chi_M)_0$, emu MKS kg^{-1} mol^{-1}	$(\chi_M)_\infty$, emu MKS kg^{-1} mol^{-1}
$(Co_3O_4)_{(s)} + 3\,(MoO_3)_{(s)} \rightarrow 3\,(CoMoO_4)_{(s)} + \frac{1}{2}(O_2)_{(s)}$	480	$4.21 \cdot 10^{-8}$	$14.66 \cdot 10^{-8}$
$(Fe_2O_3)_{(s)} + (WO_3)_{(s)} \rightarrow (Fe_2WO_6)_{(s)}$	800	$3.97 \cdot 10^{-8}$	$6.08 \cdot 10^{-8}$
$(NiO)_{(s)} + (WO_3)_{(s)} \rightarrow (NiWO_4)_{(s)}$	700	$1.07 \cdot 10^{-8}$	$1.90 \cdot 10^{-8}$

$(\chi_M)_i$ = susceptibility of equimolar mixtures at time t.

e. T. M. A. applications

Study of magnetic field effects on reaction kinetics

The idea is to compare two $\lambda(t)$ curves, one obtained with a field H_1, and the second with a field H_2.

- The first curve can be obtained continuously: in this case the field H_1 is applied to the sample throughout the reaction.
- The second curve is obtained in the same way if $H_2 \neq 0$. However, if $H_2 = 0$, no magnetic field is applied until time t_1. A quick measurement is then carried out to learn the susceptibility of the sample at this moment. Other experiments performed with other values t_i will yield the curve $\lambda(t)$ for $H_2 = 0$.

Coupled T. M. A. and TG methods for kinetics studies

For reactions where a gas is involved, combined thermomagnetic and thermogravimetric analysis gives information on the reaction kinetics case. T. M. A. corresponds to the detection of phase transformations, whereas TG follows gas adsorption or desorption. Such coupled methods can be applied to gas–solid reactions such as corrosion, solid decomposition (dehydration) or solid–solid reactions with gas emanation [9].

Study of magnetic transitions

From the $\chi(T)$ graphs, the transition points of ferro- and antiferromagnetic compounds can be detected when the magnetic balance is used for magnetochemistry studies.

Kinetic study of solid–solid reaction without gas emanation

For this purpose we have developed a thermomagnetic apparatus and the next section deals with an example of study: iron tungstate (Fe_2WO_6) synthesis. T. M. A. appears to be one of the very few methods available for such studies.

T. M. A. study of iron tungstate (Fe_2WO_6) synthesis

We have studied the iron tungstate synthesis: $Fe_2O_3 + WO_3 \rightarrow Fe_2WO_6$. As shown in Table 1, this reaction is carried out with a $\Delta\chi$ strong enough to allow the use of T. M. A.

a. Magnetic study of the reactants – experimental conditions

Tungsten trioxide, WO_3

A Koch–Light commercial product of high purity was used. This compound is diamagnetic and its experimental mass susceptibility is

$$\chi = -1.01 \cdot 10^{-9} \text{ emu MKS kg}^{-1}$$

Iron oxide, Fe_2O_3

Merck Fe_2O_3 (purity 99%) of the α variety exhibits ferromagnetic behaviour (Fig. 2) [8]. Our experimental Curie temperature is $T_C = 648°$.

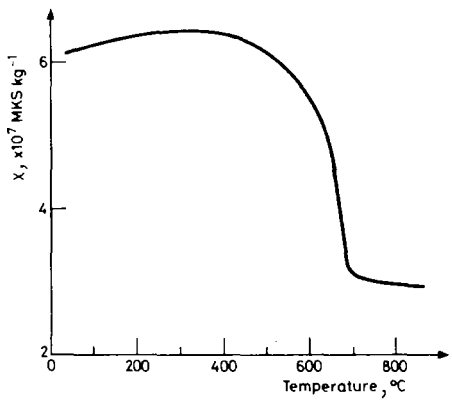

Fig. 2 Mass susceptibility of Fe_2O_3 vs. temperature

Powder preparation

Equimolar WO_3–Fe_2O_3 mixtures are ground and mixed during 10 minutes with a rotating planetary system. The WO_3 spheroidal particles (4 μm diameter) are then covered with Fe_2O_3 paricles (1 μm diameter).

Between 750° and 800°, only iron tungstate (Fe_2WO_6) is formed [13, 14], this has a paramagnetic behaviour between 25° and 825°, and it follows the Curie–Weiss law (Fig. 3)

$$\chi^{-1}_{\text{molar}} = \frac{T + 35}{2.19 \cdot 10^{-4}} \quad \text{(MKS system)}$$

until 850°; Fe_2WO_6 comprises the low-temperature phase (columbite-type structure).

b. Magnetic field effect

Two sets of experiments were carried out as described in the following section at 800° and under 10^5 Pa of air.

Table 2 gives the experimental results. Taking into account the precision of our measurements, no field influence on this reaction can be detected at 800°.

Table 2 Magnetic field effect at 800 °C under 10^5 Pa of air

t, hours	1	3	5
λ measured with $B = 0.826$ wbm^{-2}	0.22	0.35	0.48
λ measured with $B = 0$	0.24	0.32	0.46

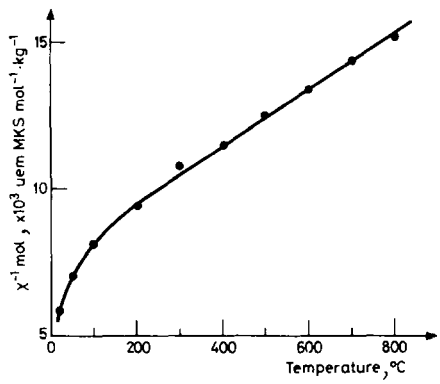

Fig. 3 Inverse molar magnetic susceptibility of Fe_2WO_6 vs. temperature

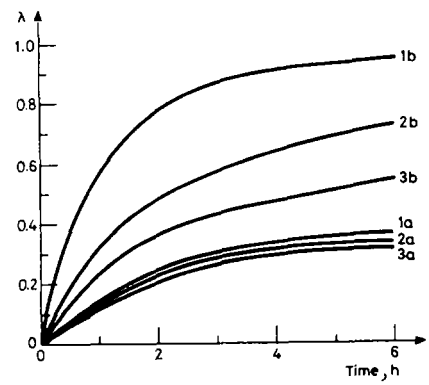

Fig. 4 Kinetics dependence on nitrogen gas pressure for (a) $T = 760°$ and (b) $T = 800°$; 1: 1.4 Pa, 2: $1.4 \cdot 10^3$ Pa, 3: 10^5 Pa

c. Influence of pressure and nature of gas on kinetics

Kinetics curves were obtained under controlled atmospheres of oxygen, nitrogen, argon or helium and at different pressures (between 1 and 10^5 Pa).

For each gas, the rate of Fe_2WO_6 formation increases as the gas pressure decreases (Fig. 4).

The rates measured at the same conversion degree ($\lambda = 0.1$) at 800° for 10^5 Pa of each gas are:

$$v_{O_2}(0.2\ h^{-1}) < v_{N_2}(0.24\ h^{-1}) < v_{A_2}(0.30\ h^{-1}) < v_{He}(0.42\ h^{-1})$$

These influences indicate that solid tungsten oxide is probably transformed into a gaseous product during the reaction. This agrees with the high sublimation pressure of WO_3 at 800°. In light of this experimental result, reaction mechanisms have been considered taking into account the gaseous transport of WO_3 [15].

Conclusion

For the continuous study of a solid–solid reaction without gas emanation, T. M. A. is one of the very simple and reliable methods whereby the real composition of a mixture can be measured. As any phase transformation can be followed by this method, wider applications can be developed, for instance studies of gas–solid reactions such as corrosion. In our work on solid–solid synthesis without gas emanation, the reactions are carried out with small ionic state modifications. T. M. A. can be expected to be much more sensitive for gas–solid reactions. Its ready coupling with thermogravimetry could give a thorough knowledge of the mechanism in heterogeneous reactions.

References

1 Z. C. Szabó, I. Batta and F. Solymosi, Proc. 4th Intern. Symp. on Reactivity of Solids, Elsevier, London, 1961, pp. 409.
2 D. Shamir and M. Steinberg, Progr. Vac. Microbalance Tech., 2 (1973) 19.
3 H. Forestier, C. R. Acad. Sci. Paris, 229 n° 1, (1947) 47.
4 H. Tzehoval and M. Steinberg, Isr. J. Chem., 22 (1982) 227.
5 J. Y. Trambouze and A. Silvent, Proc. 4th Intern. Symp. Reactivity of Solids, Elsevier, London, 1961, p. 549.
6 V. Perrichon, Ann. Chim., T4 (1969) 391.
7 M. Faraday, Experimental Researches, Vol. III, Taylor and Francis, London, 1855, 27 and 497.
8 M. M. Schieber, Experimental Magnetochemistry, North-Holland Publ. Comp., Amsterdam, 1967.
9 G. Thomas and F. Ropital, J. Thermal Anal., 28 (1983) 109.
10 R. Skorski, Nature Phys. Sci., 240 (1972) 15.
11 C. T. Peters, Nature Phys. Sci., 244 (1973) 79.
12 P. K. Gallagher, E. M. Gregory and W. R. Jones, J. Chem. Phys., 75 (8) (1981) 3847.
13 A. Trumm, N. Jahrbuch f. Mineralogie Monatchefle, (1978) 481.
14 R. S. Roth, T. Negas and L. P. Cook, The American Ceramic Society, Vol. 4 (1981) 43.
15 G. Thomas and F. Ropital, Mater. Chem. Phys., 11 (1984) 563 and 577.

Zusammenfassung — Festkörperreaktionen unter kontrollierten Druck- und Temperaturbedingungen (25—1000°) wurden mit einer magnetischen Waage verfolgt. Magnetische Eigenschaften sind charakteristisch für feste Strukturen, und die thermomagnetische Analyse (TMA) kann Veränderungen der Susceptibilität der Probe im Verlaufe der Reaktion (Susceptibilitäten neuer Phasen und noch nicht umgeformter Ausgangsverbindungen) aufzeigen. Durch kontinuierliche Messung dieser Susceptibilität nach der Faraday-Methode kann der Konversionsgrad der Synthese erhalten werden. TMA wurde zur Untersuchung des Einflusses eines Gases auf eine Fest—Fest-Reaktion, bei der kein Gas freiesetzt oder verbraucht werden lann, herangezogen. Als Beispiel wird die Synthese von Eisenwolframat angeführt: $Fe_2O_{3(s)} + WO_{3(s)} \rightarrow Fe_2WO_{6(s)}$. Bei 800° hängt die Kinetik der Reaktion von der Natur und dem Druck des Gases ab.

Резюме — Изготовлены магнитные весы для исследования твердотельных реакций при контролируемых давлении и температуре (25—1000°). Магнитные свойства являются характеристиками твердых структур и поэтому термомагнитный анализ (TMA) дает возможность определения различий магнитной восприимчивости образца в процессе протекания реакции, так как восприимчивости новых фаз и исходных соединений все еще не превращались. Непрерывно измеряя восприимчивость по методу Фарадея, можно судить о степени протекания реакции. Метод TMA был использован для изучена влияния газа на твердотельную реакцию, в которой газ не может быть выделен или поглощен. В качестве примера приведена твердотельная реакция получения вольфрамата железа по схеме: $Fe_2O_3 + WO_3 \rightarrow Fe_2WO_6$. Кинетика реакции, проводимой при 800°, зависит от природы газа и его давления.