Thermochimica Acta, 28 (1979) 113–119

DTA APPLICATION IN RESEARCHES ON PHASE EQUILIBRIA IN ALLOY SYSTEMS

R. CAPELLI, S. DELFINO, A. SACCONE, A. BORSESE AND R. FERRO
Istituto di Chimica Generale dell'Università di Genova, Genova (Italy)
(Received 23 January 1978)

ABSTRACT

A brief description is given of a simple and reliable electric furnace assembly and of its associated devices for temperature regulation and the performance of differential thermal analysis. A short outline is given of the results obtained by means of this instrument in the investigation of a number of alloy systems.

INTRODUCTION

Several devices for the performance of thermal and differential thermal analysis have been described and the literature on the various applications of these techniques is very rich. (See, for instance, the recent collection of papers edited by Wendlandt and Collins[1] and various books[2]). On the other hand it is well known that excellent pieces of apparatus, manufactured and marketed by several firms, are used for the study of different materials (metallic materials among others).

Our laboratory has been involved for a long time in the investigation of phase equilibria and in the determination of phase diagrams of alloy systems. A number of peculiar problems encountered in this process (involving the reactivity of the samples, the need for special thermal treatments, etc.) pointed out the convenience of having a laboratory-made apparatus that could be easily adapted to the different conditions encountered, both in the preparation and in the testing of the samples. This apparatus has worked very satisfactorily for many years and, owing to its reliability, easy manufacturability and low cost, a short description of it is considered worthwhile.

THE FURNACE ASSEMBLY

Generally, low voltage furnaces were used. Figure 1 shows the set-up and electric connection diagram of the furnace to the supply. The furnace supports are such that furnaces (of the carbon or tantalum resistor type) of different length and power can be easily interchanged and the whole assembly has a high degree of flexibility (for instance, it can be fastened in a vertical or horizontal position for easier connection to other devices).

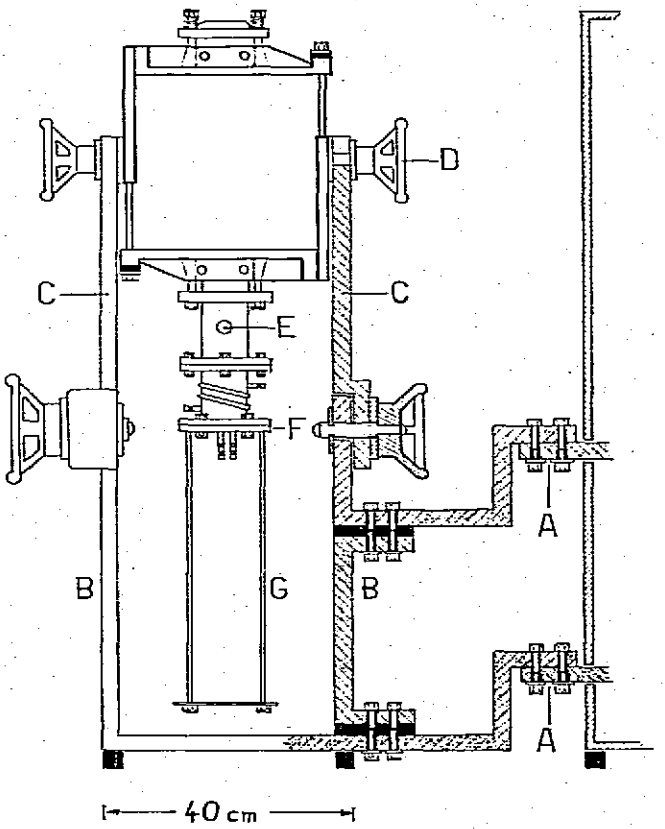

Fig. 1. Furnace assembly. A, Transformer output; B, aluminum two-legged stand (and high intensity current bus-bars); C, removable supporting bus-bars; D, fastening screws (also used for the regulation of the inclination); E, connection to the vacuum line; F, movable sample holder; G, rod guides for the vertical translation of the sample holder.

The supply has enough power to provide for quick heating of large samples to high temperatures when needed (typically, for instance, using Tammann furnaces for preparatory purposes, temperatures as high as 2000–2200 °C were reached with sample volumes of 50–100 cm^3).

Figure 2 shows the power supply regulation diagram. Its output can deliver a power of about 25 kW at a maximum voltage of 16 V. The transformer is fed by a saturable reactor which is controlled by a stabilized current, regulated by two variacs in series. The first variac, V_1, with two wipers, allows one to set the minimum and maximum bounds to power (and consequently also to temperature). The wiper on the 2nd variac can be moved manually (in the case of the furnace having to work at a fixed temperature for preparatory purposes or for thermal treatments) or it can be easily connected through a series of gears to a synchronous motor. In this way, the temperature can be gradually increased (or decreased) within the range set by variac V_1.

Typically, by operating with a furnace of the Tammann type with very fast self-cooling (which is appropriate for temperature ranges between 200 and 1500 °C) it is possible, with this apparatus, to achieve practically linear variations of tem-

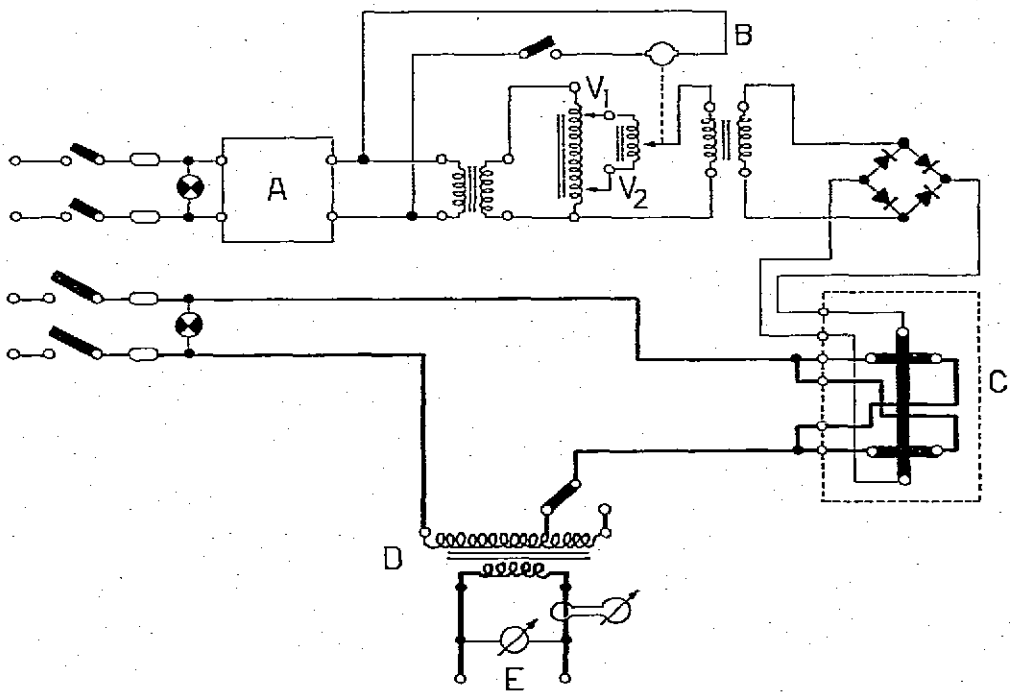

Fig. 2. Diagram of the power regulation circuit. A, Stabilized power supply; V_1, two-wiper variac; V_2, variac; B, driving motor circuit of variac V_2; C, saturable reactor; D, low voltage transformer; E, furnace circuit.

perature in intervals of several hundred degrees at rates ranging between 2 and 20 °C/min.

Figure 3 shows in detail one of the Tammann furnaces used in its DTA version. (The furnace, whose heating element is in this case of considerable length compared with the diameter is shown in its upper position on the power supply supports; in this position, the bottom of the furnace is readily accessible). The figure also shows one of the DTA devices that is housed in the furnace inside an alumina tube.

It should be observed that this alumina tube, being connected to the control line for vacuum and for the inert atmosphere, is fastened to the furnace while the sample support with its thermocouples can be extracted from the bottom by sliding on appropriate tracks. The same support holds the thermocouple reference joints which are kept at constant temperature by means of the circulating water from an ultra-thermostat. The outputs of the thermocouples are measured by a multichannel Kipp and Zonen Micrograph recorder which plots both the sample heating (or cooling) curve (on a 5–10 mV scale, possibly with zero suppression) and the differential curve (with respect to the reference material, on a 200–500 μV scale) versus time.

Typically, operating with 0.01 g at. of Au, for instance, with a rate of 4 °C/min and a base line ranging between $\pm$ 0.5 mm, one gets a differential response of 4.5 °C at the melting point. Generally, the measurements could be reproduced within $\pm$ 5–10 °C for invariant transformations.

Figure 4 shows some examples of curves obtained with this apparatus.

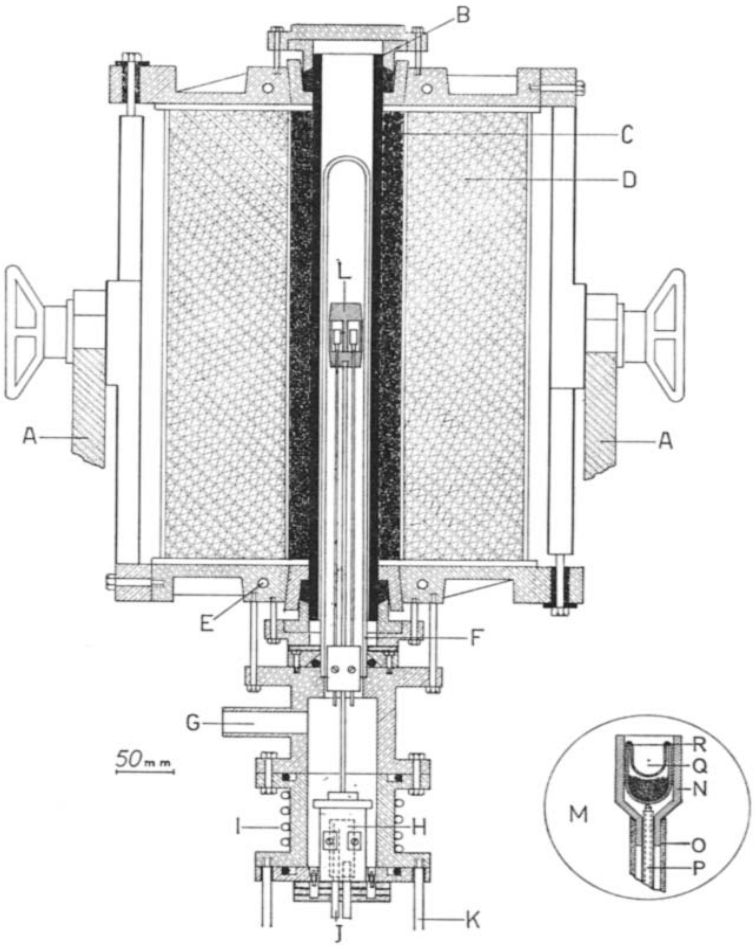

Fig. 3. Section of a Tammann type furnace and of the DTA head. A, Supports (acting also as electrical bus-bars connected at the upper and lower ends of the carbon resistor tube); B, carbon resistor; C, charcoal filling; D, refractory packing; E, cooling water; F, Al_2O_3 tube, vacuum tight; G, connection to the high vacuum and inert gas assembly; H, thermocouple reference joints (35 ± 0.1 °C); I, J, water coil connected to an ultra-thermostat; K, vertically movable supports and rod guides; L, equalizing Mo block; M, details of the sample holder; N, Mo cup; O, Al_2O_3 tubing; P, spaghetti insulator for the thermocouple; Q, Ta crucible; R, welded edge.

METALLURGICAL APPLICATION

As prevously observed, this apparatus was used by us in the investigation of alloys that, due to the high reactivity of the component metals, could not be housed in common refractory containers. In these cases, the containers were usually made from materials such as Ta or Mo and shaped as shown in Fig. 3. The small crucibles (about 0.5 cm^3 in volume) were closed under an inert atmosphere (by plasma micro-torch or arc welding). Sealed containers were considered to be necessary in order to avoid changes in the samples (e.g. slow oxidation by traces of oxygen left in the tube) or losses due to sublimation of the sample. The crucibles were mounted in the furnace

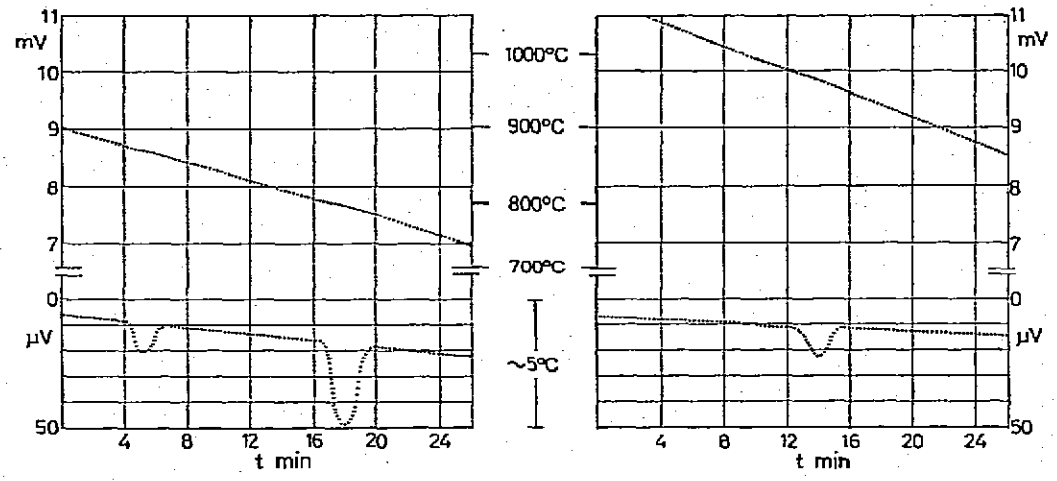

Fig. 4. Typical temperature vs. time curves (upper) and DTA curves.

either directly or in a molybdenum block for a better thermal equalization (as shown in Fig. 3).

The thermocouples used were generally of the Pt or Pt/Rh alloy type. The highest temperatures reached in normal DTA operation were around 1500°C. The thermocouples were obviously calibrated on a periodical basis by measuring the melting points of ultrapure metal samples in the same furnaces.

Even though the furnace is capable of higher temperatures, the apparatus described above was not found suitable for thermal analysis purposes at those temperatures. Under these conditions, in fact, the problems connected with the reactivity of the materials, thermocouple stability, etc. become very important and seem to obscure the results obtained by conventional DTA methods. (These problems are also well documented in the literature: see, for instance, the technique followed by Waterstrat[3] for determining the characteristic temperatures in the 1800°C range for alloys of V, Pt, etc.).

The methodology usually followed with this kind of apparatus is as follows: a first analysis is performed at a slow rate heating (2–4°C/min) on samples previously annealed for a long time. A few cooling and heating cycles are then performed ending with a rather quick cooling (even 20°C/min, which is useful, for instance, for finding melting effects while the slow speed seems to be more convenient for isolating very close effects). In many cases, the temperature is kept constant between two analysis cycles, for a few hours of annealing, in the proximity of some effect either to improve its characteristics (for instance, for peritectic transformations) or to observe its disappearance or weakening (metastable transformations, etc.). Often, it was necessary to perform different analysis cycles around the melting point in order to evaluate its correct value; this was also necessary because, in several cases, curves were susceptible to supercooling which could be as great as 100°C.

In the course of all the analyses described above, in addition to the sample temperature, the temperature difference between this sample and an inert sample was

measured (generally, the latter was a small block of tantalum of size and mass comparable with the sample). In particular cases, though, a pure substance with melting point lying in the temperature range under investigation was used as reference: for instance, Tl was used as reference for alloys with a very high Tl content in order to better evaluate the characteristics of the terminal equilibria (to discriminate between eutectic and peritectic equilibria in a very narrow ΔT range, etc.).

Of course, in all instances, the DTA data were interpreted in the light of the results obtained through chemical, metallographic, structural X-rays analysis and in some cases also direct thermal analysis (performed on samples weighing several grams).

RESULTS

The systems Ag–La[4], Ag–Ce[5], Ag–Pr[6], Ag–Nd[7], Ag–[illegible][8] and Ag–Tb[9] have been studied by means of DTA. A number of binary syste[illegible] of rare earths with In and Tl are presently under investigation (Ce–In and Nd–In[10], Pr–In[11] and Gd–In, Nd–Tl[12], Gd–Tl and Ce–Tl).

As regards the alloy systems of rare earths with Ag[13], it was possible to synthetise the thermal effect trends by applying the reduced temperature method. It proved to be of great interest since it allowed a compact description of numerous series of phase equilibria and also quantitative forecasts on unknown phase diagrams. Reduced temperatures were also related to other quantities (molar volumes, etc.) which are characteristic of the same phases.

The same device is currently also used in the examination of phase equilibria in ternary diagrams. For instance, in the examination of the Mg–Cu–Pb system[14], it was

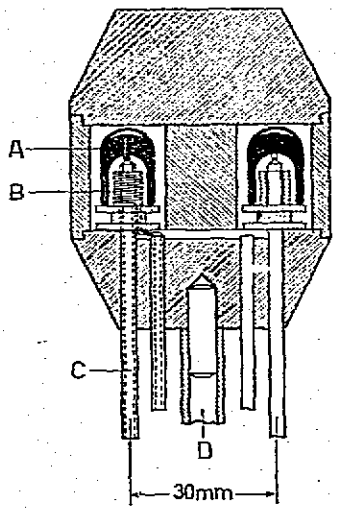

Fig. 5. Schematic drawing of a microfurnace DTA assembly. A, Test crucible; B, resistor for the electric calibration of heat effects; C, thermocouple; D, supporting rod connected to a reference joint assembly similar to that reported in Fig. 3.

possible to achieve a satisfactory resolution of numerous thermal effects generally included within a small temperature range.

DESCRIPTION OF A PARTICULAR DTA HEAD

Another DTA device, shown schematically in Fig. 5, that was used for some analyses is worth mentioning. This device is inserted, in a manner similar to that described above, in a furnace specially built for low temperatures (up to 500 °C) and it houses a small furnace inside the sample containers (very close to the differential thermocouple joints). The furnace (direct current operated and connected to a typical potentiometric and chronometric device to evaluate energy) allows the observed thermal (exothermal) effects to be simulated and their magnitude to be evaluated.

This device was, for instance, used to measure, during heating, the amount of energy released by the decomposition of metastable alloys (prepared for ultrafast quenching)[15].

REFERENCES

1 W. W. Wendlandt and L. W. Collins (Eds.), *Thermal Analysis, Benchmark Papers in Analytical Chemistry*, Vol. 2, Dowden, Hutchinson and Ross, Pennsylvania, 1976.
2 W. W. Wendlandt, *Thermal Methods of Analysis*, Wiley-Interscience, New York, 1964. P. D. Garn, *Thermoanalytical Methods of Investigation*, Academic Press, New York, 1965. W. J. Smothers and Y. Chiang, *Handbook of Differential Thermal Analysis*, Chemical Publishing Co., New York, 1966. R. C. Mackenzie (Ed.), *Differential Thermal Analysis*, Vols. 1 and 2, Academic Press, London, 1970 and 1972.
3 R. M. Waterstrat, *Metall. Trans.*, 4 (1973) 455.
4 S. Delfino, R. Ferro, R. Capelli and A. Borsese, *Z. Metallkd.*, 65 (1974) 781.
5 S. Delfino, R. Ferro, R. Capelli and A. Borsese, *J. Less-Common Met.*, 41 (1975) 59.
6 S. Delfino, A. Borsese, R. Capelli and R. Ferro, *J. Less-Common Met.*, 35 (1974) 31.
7 R. Ferro, A. Borsese, S. Delfino, R. Marazza and A. Seminara, *J. Less-Common Met.*, 35 (1974) 39.
8 S. Delfino, R. Ferro, R. Capelli and A. Borsese, *J. Less-Common Met.*, 44 (1976) 267.
9 S. Delfino, A. Saccone, A. Borsese and R. Ferro, *Z. Metallkd.*, 67 (1976) 392.
10 S. Delfino, A. Saccone, R. Capelli and R. Ferro, in C. E. Lundin (Ed.), *Proc. 12th Rare Earth Res. Conf., July 18–22 (1976), Vail, Colorado, U.S.A.*
11 S. Delfino, A. Saccone and R. Ferro, submitted to *J. Less-Common Met.*
12 S. Delfino, A. Saccone, G. Borzone and R. Ferro, *J. Less-Common Met.* 59 (1978) 69.
13 R. Ferro, S. Delfino, R. Capelli and A. Borsese, *J. Less-Common Met.*, 42 (1975) 13.
14 G. Rambaldi, D. Mazzone, R. Marazza, S. Delfino and R. Ferro, *J. Less-Common Met.*, 59 (1978) 201.
15 R. Ferro, R. Marazza, R. Capelli, G. Rambaldi and F. Baffi, *J. Less-Common Met.*, 46 (1976) 45.