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A PYROMETRIC DIFFERENTIAL THERMAL ANALYSER FOR HIGH TEMPERATURES*

F. WEHNER, E.-TH. HENIG AND H. L. LUKAS
Max-Planck-Institut für Metallforschung, Institut für Werkstoffwissenschaften, D7 Stuttgart-80 (G.F.R.)

ABSTRACT

An apparatus for differential thermal analysis to a temperature of 3400°C is described. The specimen is heated inductively with a frequency of 1 MHz either without crucible at its upper end only or in a crucible which is one of the components of the system investigated. The differential principle is applied by comparing the radiation emitted from the sample with the power fed to the sample, which is registered by a bulb coupled to the high frequency circuit. The emission of the sample and bulb are measured by two photodiodes. The different behaviour of sample and bulb is compensated electronically. Investigations in metal ceramic eutectics are given as an example.

I. INTRODUCTION

For some time there has been a great deal of interest in ceramics as high temperature materials[1], since the melting points of some of these metal oxides, metal carbides, metal nitrides, etc. are well in excess of 2000°C. For the development and application of these materials the knowledge of phase diagrams is very helpful. Thermal analysis, a commonly used technique to determine phase diagrams, is generally performed pyrometrically at these temperatures, and though thermocouples are available[2], which are capable of measuring up to 2500°C, they can only be used under particular conditions. Several apparatus were developed which determine the emission of the heated specimen by a photodiode, the current from which, calibrated against a filament pyrometer, is used to detect transition temperatures. Rupert[3–5] as well as Rudy[6] apply this method for differential thermal analysis (DTA). As a reference sample, Rupert uses the susceptor, which surrounds the sample. This apparatus requires a complicated adjusting system. Rudy heats, with his specimen, a second sample for comparison in a susceptor. For both methods the susceptor material as well as the reference sample has to be selected carefully with regard to the investigated specimen to prevent reactions. Difficulties in selecting these materials

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can be avoided by heating only the upper part of the sample in an induction coil. The lower part, which is located on a holding device, can be kept cooler and so a crucible is not necessary. This procedure was employed by Rösch et al.[7]. In this case it is difficult to compare the specimen with a reference sample, heated simultaneously, since excessively high temperature gradients operate. So Rösch registered the temperature against time (TA), and the transition temperatures are determined from the arrests. The sensitivity is increased by forming electronically the differential quotient of temperature with respect to time, and plotting it against the temperature (*T*dTA). The control of the heating current must be very precise to discriminate transition effects from effects due to hunting, since at high temperatures and consequently high electric power even small changes in control can be of the same order of magnitude as the effects. In this respect the differential thermal analysis method is more exact.

To combine the advantages of heating without using a crucible and the accuracy of the differential thermal analysis, an apparatus was devised in which an electric bulb, coupled to the RF heating circuit is used instead of a reference sample. The power, fed to the bulb, is proportional to the power, consumed by the sample, and both can be compared. The factor of proportionality, i.e., the ratio of the impedances of the sample circuit to the bulb circuit is only moderately dependent upon temperature and is nearly independent of hunting. The different behaviour of sample and bulb with changes in power has to be compensated electronically.

II. DESCRIPTION OF THE APPARATUS

Figure 1 shows the schematic construction of the DTA apparatus. The sample

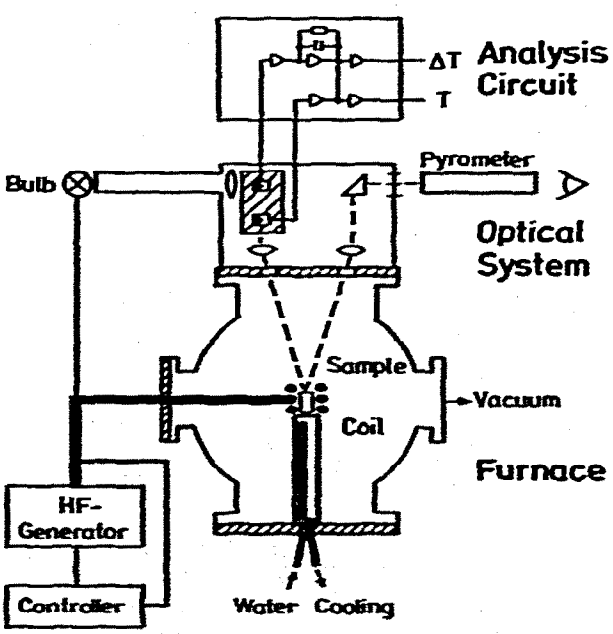

Fig. 1. Schematic construction of the differential thermal analyzer.

is located on a water-cooled device within an induction coil. Above the sample there are two optical systems, the left one of which reproduces the black body hole of the sample on a photodiode, whilst the right one is used to measure the temperature of the specimen with a filament pyrometer. A second photodiode measures the emission of the bulb, which is connected in parallel to the heating circuit. Both photodiodes are located in an aluminium block which is thermally stabilised to $-2°C$[7]. The currents from these photodiodes are fed into the thermal analysis circuit, where the temperature of the sample and the temperature difference between sample and bulb are derived and plotted on a millivolt chart recorder.

III. THE FURNACE AND THE HEATING CIRCUIT

The sample is heated in a container, which can be operated under vacuum or with inert gas. The induction coil is connected to a high-frequency generator (commercial model DS 1025/04, manufactured by Elphiac-HWG, Reichenbach/Fils, G.F.R.). The frequency depends on the coupling of the particular type of specimen and varies between 0.7 and 0.9 MHz. The power output is controlled continuously up to 25 kV by an electronic regulator (commercial model DS 8060B/04). The control delay is adjustable to a minimal time of 20 msec. The maximum error due to variations of temperature or fluctuations in the main voltage is 1% of the power output.

IV. THE OPTICAL SYSTEM

The system originally built by Rösch et al.[7] is used. An additional device was built to hold the bulb and reproduce its filament on the second photodiode. The disappearing filament pyrometer is periodically calibrated through the according optical system with a calibrated tungsten-strip lamp (Osram Wi 16/G be Z).

V. THE ELECTRIC BULB CIRCUIT

In a notch in the two collecting rails a water-cooled copper coil is inserted, which is electrically isolated. The induced current in this coil is fed along a stationary coaxial cable to the bulb. This bulb is mounted in a brass tube and a point, approx. 1 cm before the filament, is optically reproduced on one of the two photodiodes.

VI. THE THERMAL ANALYSIS CIRCUIT

The sample reacts to variations of the heating power more sluggishly than the bulb, and so to equalize this, the signal from the photodiode, which measures the emission of the bulb, has to be delayed electronically. The circuit is shown in Fig. 2.

The voltage levels of the photodiodes for the bulb (D1) and the sample (D2) are adjusted individually by the two potentiometers P1 and P2. The signals of the photodiodes are then amplified by the two similar FET operational amplifier A1

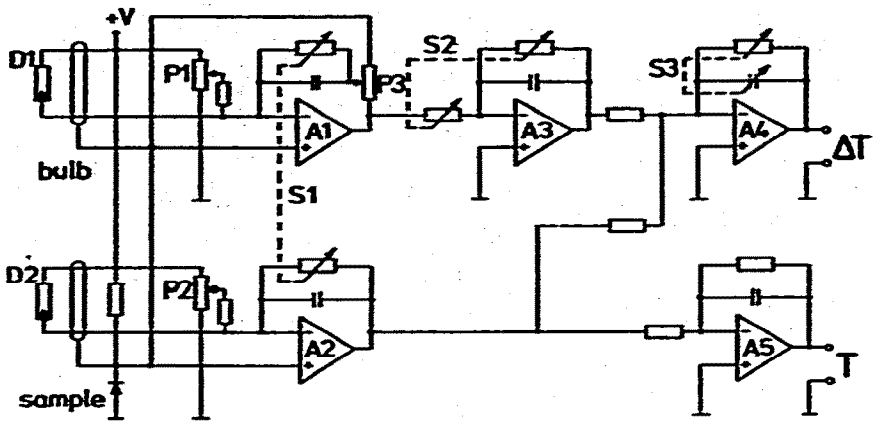

Fig. 2. Temperature- and temperature difference-analysis circuit.

and A2. By the step-by-step resistances S1, which are operated simultaneously in both circuits, five different measuring ranges can be selected. The amplifications in these ranges are chosen so that both photocurrents are roughly equalized. With the potentiometer P3 the signal of the bulb is adjusted and matched to the signal of the specimen. (Since the bulb is usually used in another temperature range than the sample, the slopes of the emission-versus-power curve of bulb and sample have to be equalized.) Both circuits include capacitors which smooth out irregularities or oscillations faster than the expected effects. The time constants of these *R–C*-feedbacks are between 0.1 and 0.4 sec. In the following circuit containing the FET operational amplifier A3, the signal of the bulb is delayed. The corresponding time constant can be adjusted by the ten-step switch S2 in the range from 0.2 to 20 sec on a logarithmic scale. This signal is subtracted from the signal of the sample by a fourth operational amplifier (A4). Its output signal then represents the temperature difference. The amplification of this difference can be changed by the five-step switch S3 in the range from 1:2 to 1:50 on a logarithmic scale. Again fast variations of the signals are smoothed by a capacitor parallel to the amplification resistances (S3). The time constant is 1 sec at all amplification ranges. Additionally the signal of the sample is inverted by the operational amplifier A5 and smoothed with a time constant of 1 sec.

VII. INVESTIGATIONS

This apparatus is used for investigations of metal–metal-oxid systems forming rod-like eutectics (e.g. ZrO_2–Ta, ZrO_2–W, Cr_2O_3–Mo, Cr_2O_3–W) in the temperature range from 1400 to 3400°C. Of interest are effects of melting, solidification and metallographic investigations after this treatment. So for this work a crucible is used (made from the same material as the investigated metal component. The crucible is located in a tungsten susceptor which is covered with a tungsten lid possessing a hole which acts as a black body. The corresponding cavity is boardered by cover, susceptor, crucible and specimen. The temperature is measured as described above. Calibration of this

TABLE 1

MEASUREMENTS OF TEST SPECIMENS IN THE DTA-APPARATUS

Specimen	*Melting point (°C)*		*Transformation points (°C)*	
	DTA	*Lit.*	*DTA*	*Lit.*
La_2O_3	2290	2320[8]	I. 2040 II. 2090	2040[8] 2210[8]
ZrO_2	2690	2680[9] 2720[8]	I. too low II. 1480	1000–1100[10] 1490[11, a]
Nb	2440	2468[12]		
Ta	3010	3000[8]		

[a] Valid for ZrO_{2-x}.

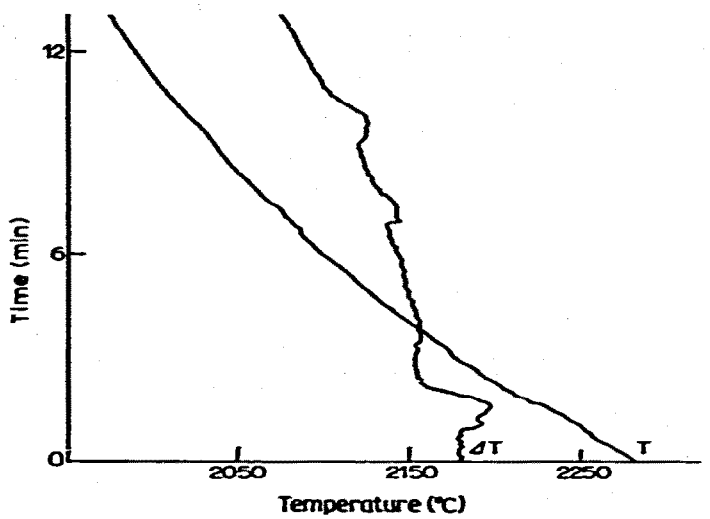

Fig. 3. Cooling curve of a La_2O_3–W mixture. T = temperature; ΔT = temperature difference; ΔT is shifted 1 mm in positive time direction.

device by measuring melting points of several materials shows that the temperature difference in the different parts of the cavity is small enough to give reliable results. The calibration points are shown in Table 1.

To demonstrate the ability of the apparatus even under difficult conditions (molten state, vaporising material, reactions during measuring — in this case $La_2O_3 + W \rightarrow 2\ La + WO_3$) the cooling curve of a hypo-eutectic La_2O_3–W alloy (approx. 0.5 g) is shown in Fig. 3. The thick line is the temperature curve, the thinner one is the ΔT-curve. This ΔT curve is shifted in the positive time direction by the indicated constant distance. The initial melting point of this mixture is determined at 2260°C, the eutectic at 2230°C. The first phase transition in the solid state is determined at

2090°C, the second at 2040°C (these values had been ascertained also for the pure oxid). The failure at 2300°C is estimated to ± 30°C.

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