Journal of Thermal Analysis and Calorimetry, Vol. 56 (1999) 233-238

ANALYSIS OF ALLOYS USING DTA AND TD METHODS WITH SIMULTANEOUS THERMOMAGNETIC STUDIES

P. Myśliński[1], *P. Kamasa*[2] *and J. Vandlik*[3]

[1]Technical University of Koszalin, ul. Racławicka 15-17, 75-620 Koszalin, Poland
[2]Research Institute for Solid State Physics and Optics, Hungarian Academy of Sciences, 1525 Budapest, P.O. Box 49
[3]Research Institute for Materials Science, Hungarian Academy of Sciences 1525 Budapest, P.O. Box 49, Hungary

Abstract

A modified thermoanalyzer for investigation ferromagnetic materials as metals and alloys is described. Conventional analog phase detection technique is replaced by specialized digital one which added some new outstanding features of the instrumentation. Samples of the material can be investigated simultaneously by three methods: differential thermal analysis (DTA), thermal dilatometry (TD) and thermomagnetometry (TMAG).

Keywords: susceptometer, thermal analysis

Introduction

The thermal analysis in combination with different measurement techniques is very fruitful from the aspect of the interpretation of the physical system behaviour observed during heating or cooling. A simultaneous measurement of different physical parameters is a very important feature of the instrumentation [1]. In this paper is described the modification of thermoanalyzer presented elsewhere [2] which permits the following kind of measurements simultaneously: differential thermal analysis (DTA), thermal dilatometry (TD), and thermomagnetometry (TMAG). The main modification is associated with alternating current (ac) TMAG where improvement in sensitivity is achieved by applying the specialised digital phase sensitive detection (DPSD) adapted to the thermomagnetic measurement [3]. The application of DPSD makes measurement reliable mainly at low frequencies where low-level magnetic signals are covered with high-level laboratory noise. The modified thermoanalyzer offers much more experimental flexibility in choice of measured physical values. Beside of TD and DTA results, the modification allows to detect changes of specific conductivity by distinguish real and imaginary part of magnetization or susceptibility. The long-time high stability allows to measure kinetics processes at certain temperature e. g. decarburization, recrystallization or oxidation.

1418–2874/99/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

Experimental

Description of the modified thermoanalyzer

The measuring cell of the thermoanalyzer was described in detail earlier [2]. The cell is provided to make experiments on sample in shape of rod max 3 mm in diameter and 30 mm in length. The electronic architecture of the modified thermoanalyzer is shown in Fig. 1. Most of the sensing devices placed in the measurement cell are connected to the computer via external instruments except sensing coil for TMAG measurement. The external instrumentation consists of precise measurement preamplifier with programmable gain. Dilatation or contraction of a sample is measured by dilatometer (VISTRONIC CE 3) [4]. A current for a radiating heater is generated by thyristor power supply controlled by temperature programmer.

Analog signals of TD and DTA are selected by analog multiplexer (PCLD 788) and measured by digital voltmeter (PCL 860S). The TMAG signal is converted by DPSD based on digital signal processing technique (DSP).

The whole system is software controlled. The user interactively creates a list of test and for each one the software determinates the voltages to be applied to the power amplifiers, programs parameters of external instruments and executes measurement procedure. The available menus are listed in Fig. 1 at the bottom.

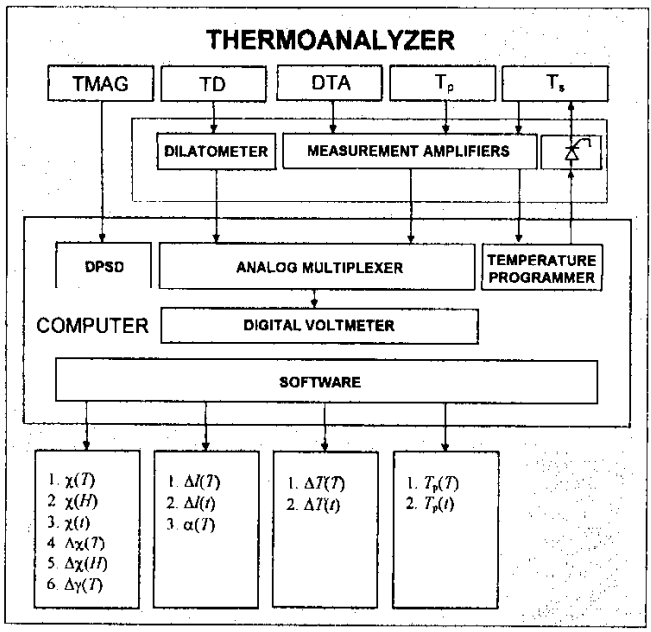

Fig. 1 Functional block diagram of thermoanalyzer for complex testing of the ferromagnetic materials

TMAG measurement

The magnetic state of the ferromagnetic sample is detected by surrounding coils. The information is taken from the induced voltage proportional to a complex permeability of the sample:

$$u(t) = (u' + iu'')e^{i\omega t}$$

$$= \alpha\omega He^{i\omega t}(\chi'' + i\chi')$$

where α is a calibration constant determined by the dimensions and geometry of the measuring sample. The values u' and u'' are the amplitude of the in-phase and in-quadrature components detected after phase detection which are proportional to χ'' and χ' respectively. Distinguish between real and imaginary part of susceptibility by applying DPSD allows to analyse behaviour of magnetization vector (Fig. 2).

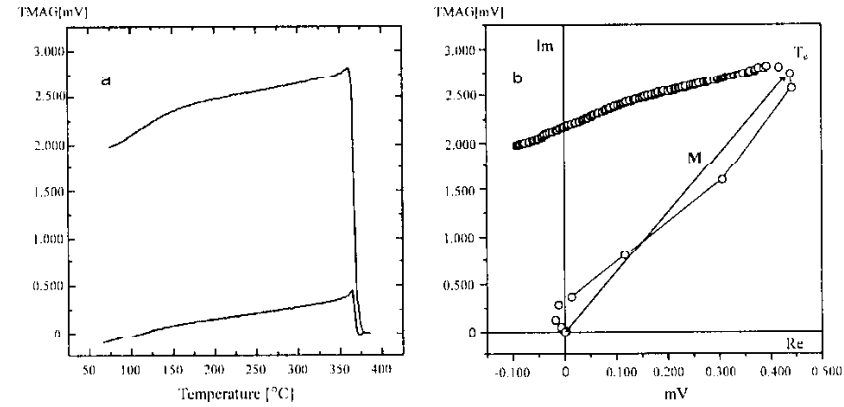

Fig. 2 Thermomagnetic curves for Ni obtained after two-phase detection during transition to above Curie temperature T_c: voltage in function of temperature a), vector of magnetization b). Frequency: 68 Hz, heating rate 30°C min^{-1}

Two-phase ac susceptibility measurement provides more information related to the physical behavior of the material around the phase transition as an influence of the electrical resistance or of the relaxation processes.

The above measurement together with precise control and measurement of the temperature gives opportunity for determination of the Curie temperature *vs.* the contents of other metals in alloys (Fig. 3). The temperature is measured by Pt-PtRh thermocouple having direct thermal contact with the sample. The stabilization is arranged by current control in feedback via software. The radiating heating system allows to control temperature in the range of 20–1100°C.

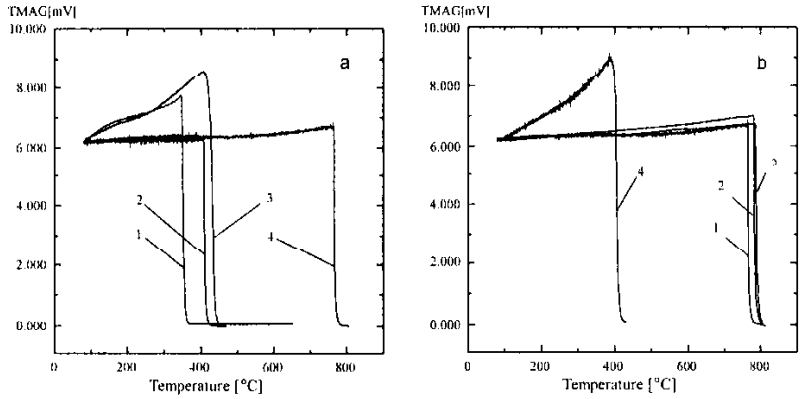

Fig. 3 Ferro-paramagnetic transition for iron alloys with different content of Ni and Cr in mass%. Curie temperatures in °C: a) 1 – Ni_{100}-359, 2 – $FeNi_{46}$-412, 3 – $FeNi_{48}$-435, 4 – Fe_{100}-769, b) 1 – Fe_{100}-769, 2 – $FeCr_{1.12}$-781, 3 – $FeCr_{3.18}$-790, 4 – $FeCr_{26}$-407

TMAG as a function of time

Thermomagnetic measurements can detect changes in the material after or during heat treatment. From the point of view of the technology, the materials testing in a laboratory is an important feature. Such process, which required long time, is for instance oxidation (corrosion). Many parts of machines work at high temperature and are exposed to active gases. The resistance to corrosion depends on the formation of a thin, closely adhering oxide film on the surface, which protects the metal

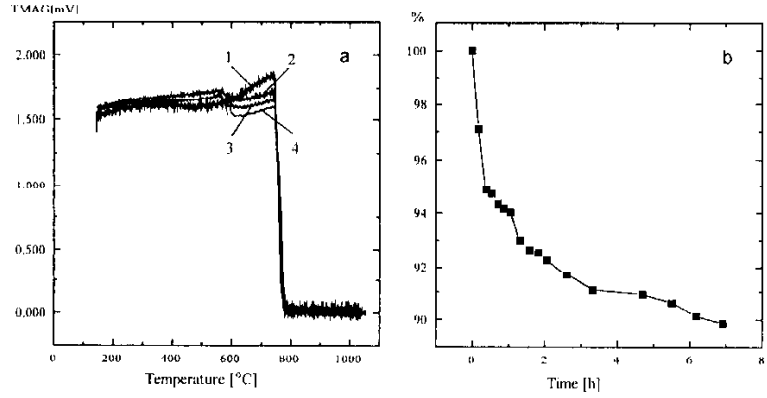

Fig. 4 Oxidation process observed by TMAG method: a) TMAG curves for iron sample: 1– original sample, 2, 3, 4 – after 2, 4, 6 h of annealing at 1100°C respectively, b) relative decrease of the magnetization during continuous annealing at 1100°C, during measurement the sample was cooled down to the ferromagnetic state to 625°C

from further attack. Some oxides are ferromagnetic having specific Curie temperatures and can be detected by TMAG. In Fig. 4a are shown TMAG curves for an iron sample annealed at 1100°C every two hours. As the time of annealing increases, a Curie point at 585°C can be observed because of formation the oxide Fe_3O_4 on the surface. This oxide protects the surface against direct contact with oxygen and relative speed of oxidation decreases (Fig. 4b).

Complex thermal analysis

During magnetic phase transitions detected by TMAG method it is able to measure simultaneously thermal behaviour and dilatation of the investigated material. The thermal information is obtained from the DTA curve by measuring the temperature difference between the investigated and reference Cu sample using differential connected Pt/PtRh thermocouples. The reference sample is the same shape as investigated, positioned at the equivalent place in the radiating heater. In the TD measurement two sensors of linearly variable differential transformer are used. Dilatation of the specimens is transferred to the sensors by means of silica glass rods.

In Fig. 5 results from simultaneous measurement by TMAG and DTA and TD methods are shown. In the Fig. 5a is shown negative peak of temperature detected for a highly pure Ni sample near the critical point T_c. Similar analysis supplemented by dilatometric measurement for Fe sample is shown in Fig. 5b. The DTA curve shows anomalous thermal behaviour at T_c point. At temperature 910°C is observed thermal and dilatometric discontinuity (curves DTA and TD) associated with transition from body-centred to face-centred cubic structure of Fe. The TMAG curve not only indicates ferro-paramagnetic transition of Fe sample at T_c=769°C, but at 585°C the Curie point of the oxide Fe_3O_4 is observed.

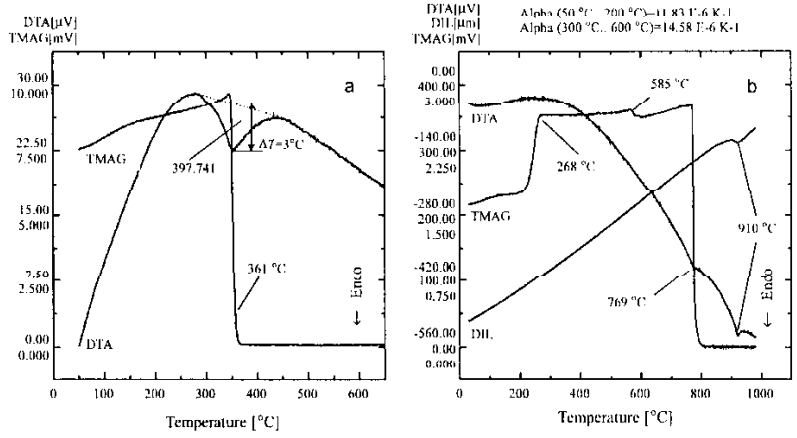

Fig. 5 Results of simultaneous measurement by DTA, and TMAG of Ni sample a), DTA, TMAG and TD of Fe sample b). Heating rate 20°C min^{-1}

Conclusions

The results presented above underline the experimental possibility of the developed thermoanalyzer. Several examples from the measurement are the most significant in studying properties of the ferromagnetic materials using thermoanalysis methods. Contrarily to classical device, our solution enables ease to choose useful electromagnetic working conditions as frequency and magnetic field strength. In addition, the excitation and detection system for TMAG measurement allows to choose special measurement conditions as arbitrary programmable waveform of excitation and detection at any harmonic frequency. Built-in function of electronic compensation of the measurement bridge increases sensitivity.

Reference

1 P. K. Gallagher, Thermomagnetometry, Proc. 11th ICTAC Philadelphia, 1996, M. Y. Keating (Ed.), Vol. 1, Akadémiai Kiadó, Budapest, 1996 p. 33.
2 P. Myśliński, W. Precht and J. Staśkiewicz, J. Thermal Anal., 35 (1989) 193.
3 P. Kamasa, L. K. Varga, E. Kisdi-Koszo and J. Vandlik, Rap. Quenched Mater. Supplement, (1997) 280.
4 FWP VIS SA, Warsaw.