Thermochimica Acta, 83 (1985) 17–21
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

ANOMALIES IN THE THERMAL EXPANSION OF FERROMAGNETIC METALS AND ALLOYS

W. Hädrich
NETZSCH-Gerätebau GmbH, D-8672 Selb/Bayern

ABSTRACT

During the transition from the ferromagnetic to the paramagnetic condition unsteady changes of dimensions occur, which, however, compared to the usual thermal expansion or to crystalline transitions are small (/1/, /2/) and therefore difficult to detect with conventional dilatometers. This paper shows such expansion anomalies for different ferromagnetic pure metals and alloys in the range of their Curie temperatures. The measurements were made with a modern differential dilatometer (amplification max. 250.000, resolution ± 20 nm). This allows, relatively easily, exact qualitative and quantitative measurements of such phenomena.

INTRODUCTION

Already in 1937 Louis Néel described the non-linearity of the thermal expansion of ferromagnetic metals and alloys due to the change of coupling forces between the magnetic layers. For the Curie temperature he states that the discontinuity of the expansion coefficient, $\Delta\alpha_\theta$, can be represented as:

$$\Delta\alpha_\theta = \left(\frac{d\sigma^2}{dt}\right)_\theta \left[\frac{n_1}{4Ad} + \alpha\theta\left(\frac{n_2}{A} - \frac{n_3}{2B}\right)\right]$$

σ = $N \cdot q_{/}u$

θ = Curie temperature

A,B = coefficients of compressibility

$$n_1 = \sum_i \frac{2p_i l_i}{d} \cdot \frac{\partial u_i}{\partial l_i}$$

$$n_2 = \sum_i \frac{p_i l_i^2}{d^2} \cdot \frac{\partial^2 u_i}{\partial l_i^2}$$

$$n_3 = \sum_i \frac{p_i l_i^3}{3d^3} \cdot \frac{\partial^3 u_i}{\partial l_i^3}$$

N = Avogadro's number

q = number of spin parallel orientated electrons per atom

$/u$ = Bohr's magneton

l_i = atomic distance at absolute zero

$2p_i$ = number of neighbour atoms in distance l_i

$u_i = w_i \cdot \frac{1}{N\mu^2}$, for w_i

$w_i = \frac{n\sigma^2}{2q^2}$, n = molecular field coefficient

It is remarkable that the change of the expansion coefficient does not always take place in the same direction but depends on the distance between the magentic layers, d - 2r, where d is the reaction radius of the magnetic layers.

A difference $<$ 1,31 nm results in an unsteady increase of α shortly before reaching the Curie temperature, a difference $>$ 1,31 nm a decrease.

EXPERIMENTAL

The measurements for the paper discussed were made with a modern, commercially available differential dilatometer, the data stored on disk and evaluated with a computer.

The differential dilatometer measures the change in length of a sample body compared to a reference body (Fig. 1). This is detected by two scanning rods, where one is connected to the core of the displacement transducer and the other to the transducer coil. By use of a frictionless support of the scanning rods by trapezoid spring systems in tandem arrangement, measurements with up to 250 000 times amplification can be reproducibly realized. The required small error limits demanded amplifiers with exceptionally good linearity.

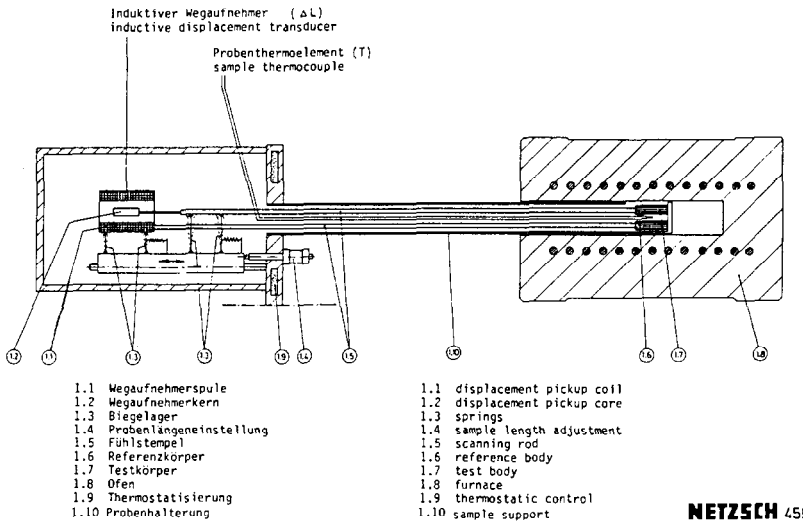

Fig. 1 Differential Dilatometer Fig. 402 ED (Function Principle)

All tests were performed on 25 mm long samples in an atmosphere of catalytically cleaned helium with a heating rate of 5 K/min. Comparison measurements of the following materials were made: -

Sample	Reference
nickel	Al_2O_3
nickel	cobalt
iron	Al_2O_3
iron	permenorm 5000 H3
mumetal	trafoperm N3

The selection of alloys [+)] was made considering the ICTA Certified Reference Materials for thermogravimetry GM-761, the pure metals were available in a purity $\geq$ 98%.

Compared to the individual references the following relative expansion coefficients and Curie temperatures Θ in Kelvin result: -

sample	reference	α_1	α_2	$\Delta\alpha$	Θ
nickel	Al_2O_3	+ 9,90	+ 9,20	+ 0,70	647
nickel	cobalt	+ 2,50	+ 1,50	+ 1,00	645
iron	Al_2O_3	+ 2,20	+ 3,85	- 1,65	1047
iron	permenorm[1)]	-	-	-	-
mometal	trafoperm	+ 0,80	+ 0,70	+ 0,10	686
permenorm[2)]	iron	- 6,75	- 3,50	- 3,25	729
trafoperm[2)]	mumetal	- 3,00	- 2,25	- 0,75	1047
cobalt[2)]	nickel	- 0,70	+ 0,35	- 1,05	1393

α_1 : $\alpha_{(0 - 20\ K)} \ldots 0 \times 10^{-6}$ α_2 : $\alpha_{0 \ldots (0 + 20\ K)} \times 10^{-6}$

$\Delta\alpha$: $(\alpha_1 - \alpha_2) \times 10^{-6}$

[1)] not calculable due to the simultaneous transformation of reference

[2)] sample and reference mathematically exchanged

Deviations of the Curie temperatures compared to literature values are due to the following reasons: -

1. Here the temperature at point of inflection on the dilatation curve was taken as Curie temperature.
2. The heating rate of 5 K/min for such measurements is relatively high.
3. The pure metals used showed considerable residual impurities.
4. The values determined by ICTA for the alloys apply only for one exactly defined batch.

[+)] We thank Messrs. Vakuumschmelze GmbH, Hanau for providing the samples.

An impressive example of the presentation of results is shown in the following figure:

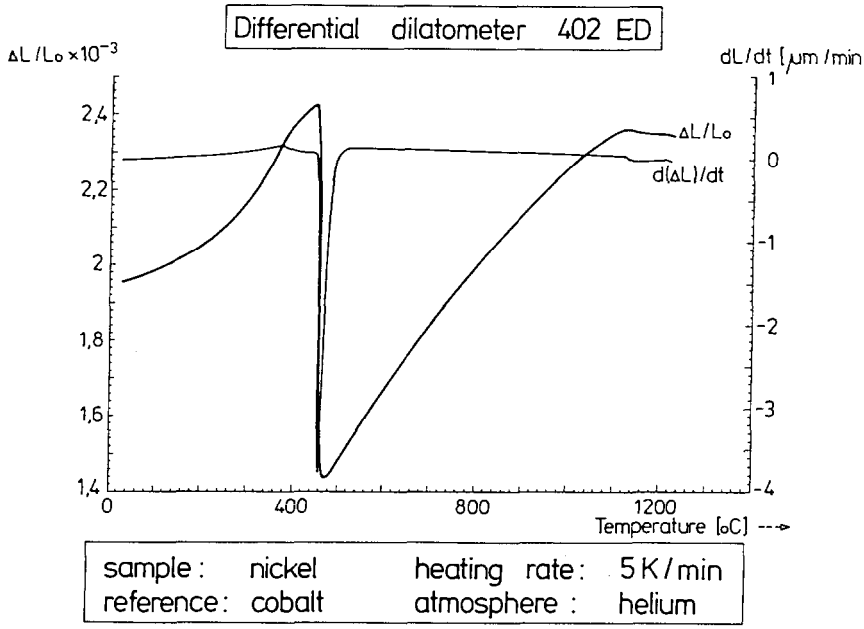

Fig. 2

It shows a computer plot of the measurement nickel against cobalt. One can clearly see the two magnetic transitions of sample and reference as well as the much higher $\alpha \rightarrow \beta$ transition (hexagonal $\longrightarrow$ cubic) of cobalt. Nickel shows an increase of expansion coefficient directly before the magnetic transformation, cobalt, however, a decrease which in the Δl curve occurs in the same direction because cobalt is used here as the reference.

This behaviour of cobalt could not be experimentally proved by Néel and Chevenard but was, however, forecast by theory (/1/).

The time deviated curve $\frac{d(\Delta l)}{dt}$ is an excellent aid to interpretation. This is particularly clearly shown in the measurement of mumetal against trafoperm. Here the change of α is a good ten times smaller than for the other measurements. Nevertheless the $\frac{d(\Delta l)}{dt}$ curve shows this effect very clearly. The curve is very reminiscent of a DTA curve for 2nd order phase transitions.

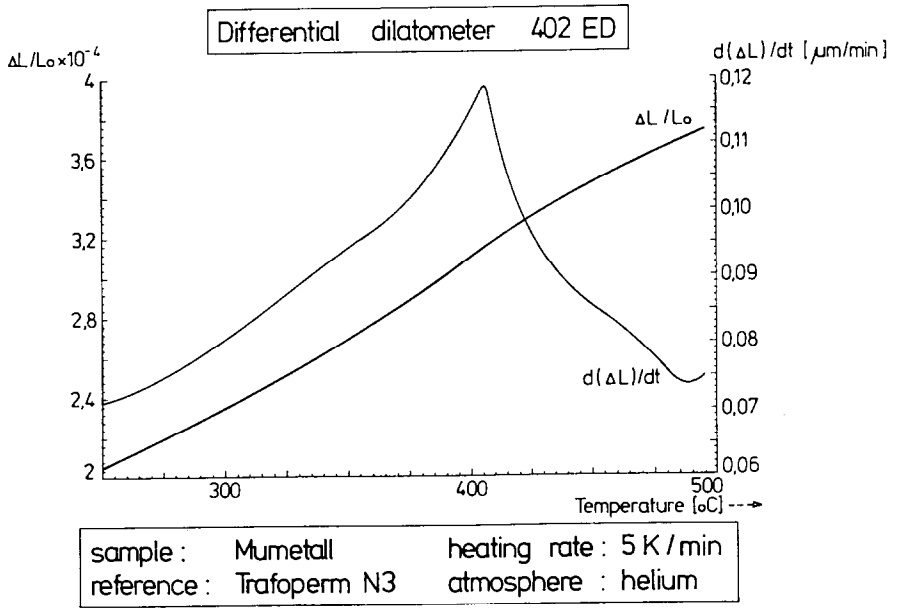

Fig. 3

This work clearly demonstrates that a commercial instrument, the differential dilatometer, is now available, able to routinely detect minimal dimension changes. It also allows routine measurement of unsteady interatomic processes which take place without crystal structure change. This could, therefore, become very important for the research and development of alloys.

LITERATURE

/1/ L. Néel, Etudes sur le moment et le champ moléculaire des ferromagnetiques, Ann. Phys. 8 (1937), 237 - 308.

/2/ H. Pascard, A. Globus, Volume anomaly in ferrimagnetism, J. Physique Lettres 42 (1981) 319 - 322.