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MEMORY ALLOYS TO BE USED AS ENTHALPY STANDARDS ?

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Abstract

Two-way memory alloys show a reversible structural transformation which is linked up with transformation heat. At a heating rate of 5 K/min the scatter of the transformation heat of a thermally stable Ni-Ti alloy is smaller than ± 1 %. The inhomogeneous predeformation due to torsion results in a reaction interval about 90 K in width. A Cu-Al-Mn alloy homogeneously deformed by rolling shows a reaction interval 30 K in width. Reaction temperature and reaction interval can to a certain extent be set on the basis of the composition and the kind and degree of predeformation, so that the production of "tailored" enthalpy standards is conceivable which resemble the effect to be investigated. The production of such standards would, however, demand great sophistication and their use would be subject to certain restrictions.

Introduction

The enthalpy calibration of scanning calorimeters is carried out either via heats of fusion (of metals) or via the specific heat capacity of a solid. Only few calorimeter types allow an electric calibration device to be fitted at the sample site, by means of which the thermal effect can be repeated in a calibration test. Calibration with the aid of heats of fusion is an extrem unsteady-state method, that executed with specific heat capacities is a quasi-steady-state method. Most of the reactions investigated do not develop like the melting of a metal, nor is the reaction heat flux almost constant for a prolonged period. The smallest systematic uncertainties result when the shapes of the measurement

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curves are similar during measurement and calibration. Where e tric, adaptable calibration is impossible, it would be expedie to have calibration material with the following properties at one's disposal:

Solid state reaction;
Selectable reaction temperature;
Selectable reaction interval.

The two-way memory alloys meet these requirements to a certain extent. Although a final decision as to the suitability of suc alloys as calibration material cannot be taken yet, first inve tigations will be described in the following.

Memory alloys

Fig.1 (according to /1/) shows the stress-strain curve of an Ni-Ti memory alloy. After elastic elongation the sample can be plastically elongated at almost constant stress. This is due t the fact that during deformation a second phase, the so-called "stress-induced martensite", develops in the initial structure This martensite does not recede when the stress is reduced, ho ever, it does so when the alloy is heated beyond a definite temperature. In the case of an Ni-Ti alloy a plastic elongatio of up to approx. 8 % can be cancelled by heating. By a special "training" - a cyclic thermo-mechanical treatment - a "two-way memory effect" can be imposed on the material /1/. If a traine predeformed sample is heated, the deformation recedes but develops again during subsequent cooling. This means that no external mechanical stress is required for the reversible deformati but that heating and cooling are sufficient. Apart from the Ni- alloy a number of other memory alloys are known (see e.g. /2/ Fig.2 shows the thermal expansion of a bar made from an Ni-Ti alloy predeformed by torsion (54.4 % Ni, 45.6 % Ti, 0.1 % C, <0.1 % Fe, 0.09 % O_2) during heating and cooling. The transformation shows a hysteresis.

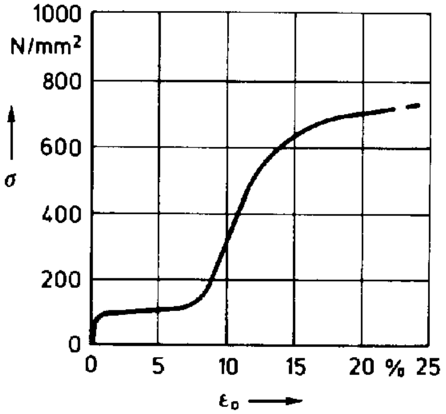

Fig. 1:

Stress-strain curve of an Ni-Ti wire 2 mm in diameter (according to /1/)

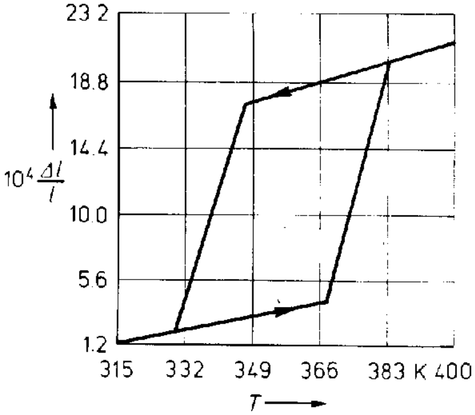

Fig. 2:

Thermal expansion of an Ni-Ti bar (10 mm in diameter) predeformed by torsion, as a function of temperature (mean values from three measurement series, heating or cooling rate, respectively: 0.2 K/min)

Caloric measurements

After a short-time storage of the Ni-Ti samples (378 mg) in liquid nitrogen at a heating or cooling rate resp. of 5 K/min a heat of transformation of 26.7 J/g was measured with the aid of a differential power scanning calorimeter (DSC-2, Perkin Elmer), the standard deviation amounting to 0.2 J/g (0.7 %). Fig.3 shows a measurement curve. The peak area was determined according to planimetry as well as with the aid of a computer. Owing to the uncertainty of the integration limits the maximum uncertainty of the computational determination of the area amounted to ± 1 %, the uncertainty of the planimetric determination being estimated at ± 2 %.

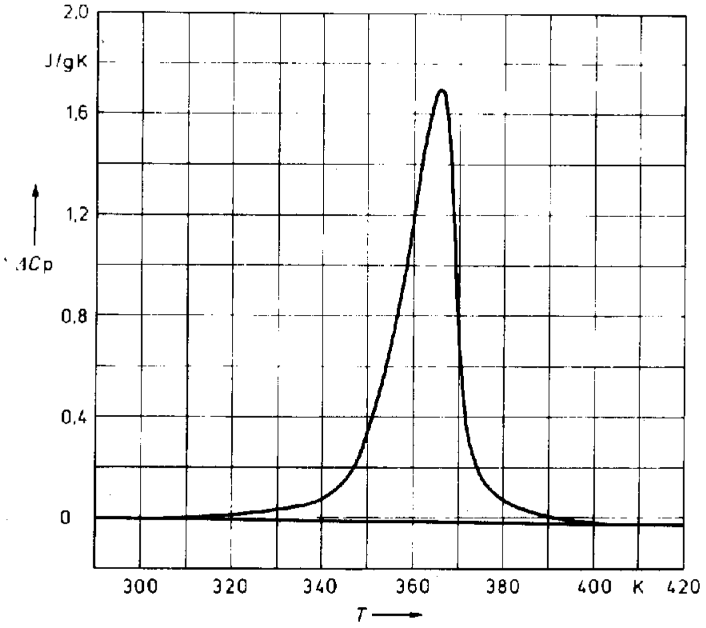

Fig. 3:

Change of the specific heat capacity of an Ni-Ti sample during transformation.
Heating rate 5 K/min, sample mass 378 mg, pretreatment: 10 min in liquid nitrogen.

The peak temperatures (365 K during heating) are repeatable to within ± 0.5 K. The peak width at the base line amounts to approx. 90 K, the half-width is approx. 17 K whereas the difference between the peak temperatures during heating and cooling (hysteresis) is more or less 45 K. Two years later, further measurements were carried out at heating rates between 1.25 K/min and 10 K/min. They showed a slight dependence of transformation heat and peak temperature on the heating rate, so that the mean value of 27.6 J/g lies within a range of dispersion having a width of 4.5 %. The deviation of 3.3 % of the mean values of both measurement series can - for the most part - be explained by the exchange of the measuring system carried out in the meantime, and its subsequent calibration.

A ring with an inside diameter of 4 mm was manufactured from the disc-shaped sample (6 mm in diameter). The first two measurements on this sample made with a heating rate of 5 K/min yielded transformation heats of 20.3 J/g and 22.1 J/g resp.; the subsequent 9 measurements yielded a mean value of 23.7 J/g with a standard deviation of 0.4 J/g (1.8 %), the relatively great dispersion being due to the slow increase in the transformation heat during successive measurements. These results allow two conclusions to be drawn:

- After mechanical treatment the transformation is reversible only after several cycles;
- In an inhomogeneously predeformed sample the heat of transformation is locally different.

Summarizing it can be stated that, with a heating rate of 5 K/min, the transformation heat of a thermally stable Ni-Ti sample can be determined with a dispersion of less than ± 1 %, the standard deviation being used as a measure of the dispersion. When the uncertainty of the determination of the peak areas is included, the stated dispersion may well be characteristic as total uncertainty of measurement, too. The dispersion is greater with varying heating rates; the same applies to a mechanically treated sample whose thermal behaviour is not yet stable.

The broad reaction interval of about 90 K at the basis is the special feature of the measurement results obtained for this memory alloy. The large peak width is a consequence of the inhomogeneous torsional deformation of the sample during the "training", for the transformation temperature increases with the degree of deformation /1/, so that the outer layers which show a stronger deformation react only at temperatures higher than those at which the slightly deformed core reacts.

Rolled Cu-12.5 % Al-4 % Mn was investigated as an example of a memory alloy with narrow reaction interval. With a heat of transformation of 6.4 J/g (standard deviation 0.2 J/g) and a peak temperature of 308 K (35 $^{\circ}$C), a peak width of 30 K resulted at the base line (half-width approx. 5 K).

The memory alloys generally show a strong dependence of the tra formation temperature on the composition. For example, the peak temperature of an equally rolled Cu-12 % Al-4 % Mn alloy turned out to be 373 K (100 °C). The transformation temperature of an Ni-Ti alloy also depends strongly on the concentration; with a 2 % change of the concentration, the transformation temperature changes by more than 200 K (according to /1/).

Conclusions

Two-way memory alloys may be considered interesting potential ca bration materials for scanning calorimeters as they offer the following advantages which allow the calibration to be rendered similar to the measurement proper:

- Setting of the desired reaction temperature by choosing an appropriately composed alloy;
- setting of the desired reaction interval by the nature and degree of plastic deformation during "training".

Mention must be made of the following restrictions:

- Only a definite batch of an alloy pretreated in a specific way may serve as calibration substance;
- mechanical aftertreatment of inhomogeneously predeformed samples is impossible;
- prior to the measurement a definite state must be established, e.g. by immersing the sample into liquid nitrogen;
- the sample must be measured in the pan as it may "migrate" during transformation.

The variability as regards reaction temperature and interval is thus linked up with increased sophistication during preparation and certain restrictions of use.

In this paper, only first results have been reported. A great many experiments (long-term stability, dependence on heating rates, etc.) are still required in order to come to a final decision on the suitability of these alloy as calibration materials.

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