QUANTITATIVE DIFFERENTIAL THERMAL ANALYSIS FOR DETERMINING THE STORED ENERGY OF COLD WORKED COPPER[*]

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ABSTRACT

By means of quantitative differential thermal analysis, it is possible to measure the stored energy of cold worked metals. Comparative measurements on standard copper samples, performed by various laboratories, show that it is most probable that the measuring accuracy of the calorimeters depends on the sample shape. A systematic investigation of the effect of foreign atoms showed that the stored energy can increase or decrease according to the type of atom added. The examination of samples rolled and stressed by torsion in various ways showed a strong dependence of the stored energy on the details of the deformation process.

INTRODUCTION

Differential thermal analysis (DTA) has for a long time been a standard method of investigation in metallurgy. To the present day, it is principally employed in the elucidation of the phase diagrams of metallic systems, i.e., alloys. Indeed, even some 45 years ago the quantity of heat converted in a sample was determined from the area between the measured curve and the baseline (according to ref. 1). However, in general, quantitative investigations showed large deviations since this area was strongly dependent upon the sample parameters and the design of the measuring apparatus. An important step in the direction of quantitative DTA was the inclusion of the detection thermocouples in a fixed component of the apparatus, e.g., the sample or reference sample container, respectively, that is, their removal from the sample material[2]. In this way it was achieved that the density and thermal conductivity of the sample had hardly any effect on the area of the measuring peak. Equally important was the realization of heat-transfer conditions within the apparatus which depend in a reproducible way on the temperature alone.

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[*] Presented at the 2nd Symposium of the German Society for Thermal Analysis held at the University of Konstanz from 5–6 July, 1976.

FUNDAMENTALS OF QUANTITATIVE DTA

With the aid of quantitative DTA enthalpy changes ΔH are measured via anomalies in the specific heat c of the sample:

$$\Delta H \equiv \int dQ = \int c(T)dt \qquad (T = \text{temperature})$$

Since no direct measuring procedure for heat quantities Q exists, one measures these latter using temperature differences ΔT which produce a thermal flux dQ/dt on flowing through a thermal resistor:

$$\Delta T \sim dQ/dt \qquad (t = \text{time})$$

With this ΔH can be calculated from the area between baseline and the $\Delta T(t)$ curve:

$$\Delta H = K(T, \ldots) \int \Delta T(t)dt \qquad (K(T, \ldots) = \text{calibration factor})$$

In the apparatus for quantitative DTA, differential thermoelements are connected between sample and reference sample container, which measure the difference in the thermal flux from the furnace to these two containers as a thermoelectric potential. The heat transfer between furnace, sample and reference sample need not be accurately known, but it does have to be exactly reproducible and only dependent on temperature. Only then can an apparatus or calibration factor $K(T)$ be associated with each temperature, provided the remaining experimental conditions stay the same (e.g., type of gas and gas pressure). Since the heat-transfer conditions in a practical measuring device are extremely complex, particularly at boundary surfaces, no sufficiently accurate method exists by which $K(T)$ may be calculated[1]. For this reason the relationship between the peak area and the heat converted in the sample is established experimentally in every case, i.e., $K(T)$ is determined by calibration measurements.

STORED ENERGY OF COLD WORKED METALS

Metals may be cold-worked by hammering, rolling or other means of deformation. Here deformation work has to be expended. The greater part of this work is already converted into heat during the deformation, a small portion, about 10%, remains stored in the metal. This portion is denoted "stored energy"; it is the inherent energy of the lattice defects created by cold working. For deformation at room temperature we are chiefly concerned with dislocations. These dislocations may be removed from the metal again by heat treatment, they "heal" and their inherent energy is released. A new structure of undeformed grains is then created. The driving force for this process (denoted "recrystallization") is the stored energy. After recrystallization the originally deformed metal is in an undeformed state of lower enthalpy. The stored energy, released during recrystallization, is for copper of the order of 0.1 to 1.5 J g^{-1}. The stored energy is thus a factor 10^2 to 10^3 smaller than the heat generally observed in chemical reactions. Thus, it is not very surprising that

the values given in the literature differ strongly[3]. The deviations of comparable measurements are often much larger than the errors of measurement quoted by the authors. In the following, using certain chosen, more recent results, it shall be shown what evidence is available today on the stored energy of deformed copper, obtained with the aid of quantitative DTA measurements.

COMPARATIVE MEASUREMENTS OF THE STORED ENERGY

To compare the experimental results of various laboratories, rolled and torsion copper samples, respectively, produced by one laboratory in each case, were sent to four different laboratories[4]. For the measurement of the stored energies, self-made and commercial apparatus were used. The results are shown in Fig. 1. In the case of the rolled copper samples three of four results are in excellent agreement; this value may be taken as the "true" value of the stored energy. The measuring values of the torsion samples were scattered more uniformly about the mean value than was the case for the rolled samples. For the number of measurements considered, this value may be regarded as the "true" value with an error limit of $\pm$ 33%.

The essential reason for the scatter of the measured values of the various laboratories is considered to be that the different calorimeters require diverse sample shapes. Hence, the most suitable measured samples had to be produced using the standard sample supplied. This was not possible for calorimeter No. I for the rolled sample for instance, and for this reason the error of measurement and the deviation from the mean value here was particularly large. From the torsion standard samples
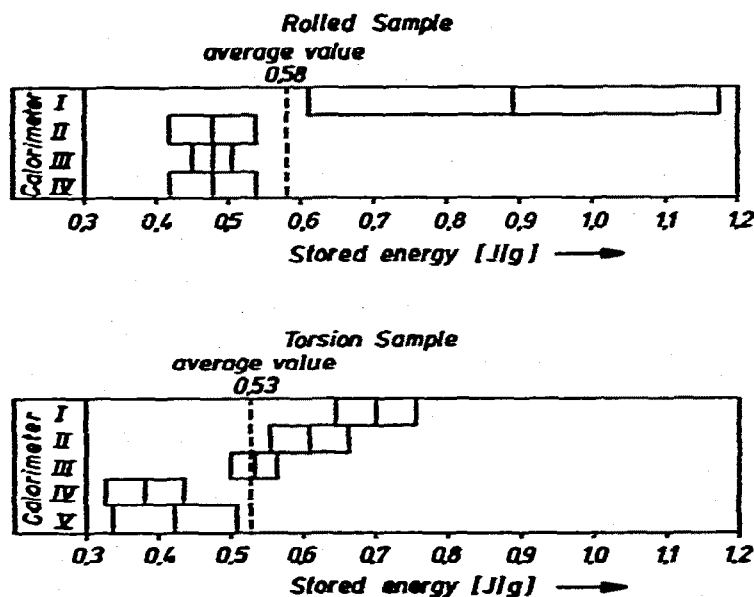

Fig. 1. Schematic representation of the results of different working groups on rolled and torsionally stressed copper samples. The length of the bar corresponds to the measuring error quoted by the author for the respective calorimeter. After ref. 4.

more or less satisfactory, though not always optimum, samples could be produced for all calorimeters; this was expressed in uniform scatter of the measured values about the mean value.

These experiments show that comparative measurements with different calorimeters are of limited value even when using "standard samples", since the sample shape can affect the measuring accuracy.

THE EFFECT OF VARIABLES ON THE AMOUNT OF STORED ENERGY

The amount of stored energy depends on the deformation conditions and the chemical composition of the metal.

Numerous experimental results are available[3] which were obtained for various metals deformed in different ways. Whether an unequivocal relationship exists between the amount of stored energy and the parameters defining it, and what character it would have, is to this day unknown. One reason for this is that, even for simple types of deformation (e.g., tension), the relationship between the density of lattice defects and the degree of deformation is only known for small degrees of deformation. For high degrees of deformation as well as for complex types of deformation (e.g., rolling), this relationship is unknown. Another reason is that the effect of foreign atoms on the density and arrangement of lattice defects is hitherto unknown. A first step towards the explanation of this effect was the systematic investigation of the influence of small quantities of foreign atoms on the stored energy of rolled single crystals of high purity copper, using quantitative DTA[5]. Thereby it was discovered that the stored energy can increase or decrease according
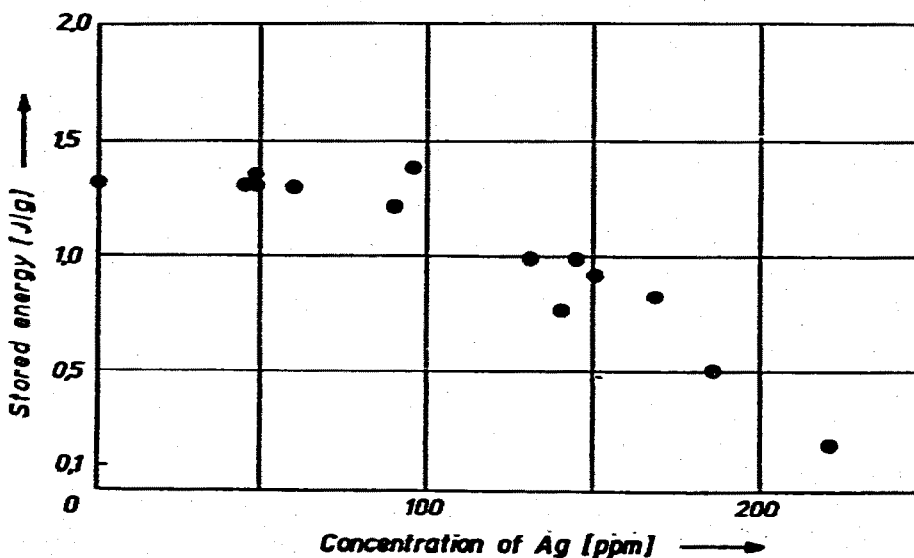

Fig. 2. Stored energy of copper–silver single crystals versus silver concentration. Initial orientation (112)[111]; rolled to a thickness reduction of 98%. After ref. 5.
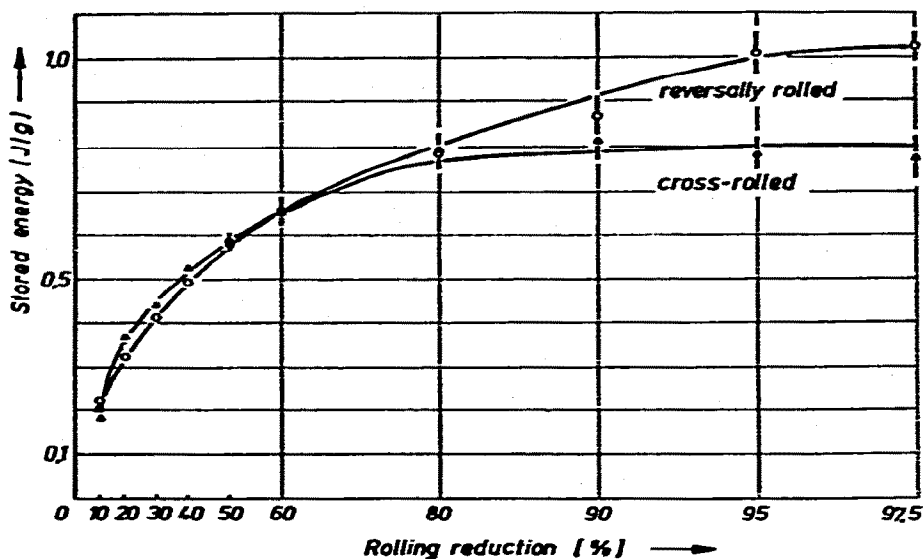
Fig. 3. Stored energy of reversally and cross-rolled copper as a function of the rolling reduction.

to the type of additionally alloyed foreign atoms. For example the stored energy decreases on addition of silver (Fig. 2).

In addition to the purity of the metal, the type and degree of deformation have great influence on the amount of stored energy. Some more recent measurements of the stored energy of rolled and torsion copper shall be presented in the following.

Polycrystalline copper (purity 99.997%) was rolled to various degrees in two different ways. First it was reversally rolled, i.e., the sample was turned 180° about the sheet normal axis after every reduction step before rolling was continued. Then it was cross-rolled, i.e., the sample was turned 90° after every reduction step. The stored energies of the reversally and cross-rolled samples are plotted in Fig. 3 as a function of the rolling reduction (rolling reduction is the reduction of the initial thickness of the rolling strip in %). The stored energy initially increases with the rolling reduction and levels off to a constant value for high rolling reduction. The result for relatively impure copper, that cross-rolled samples store less energy than reversally rolled samples[6], was confirmed here for purer copper at higher rolling reduction. It is surprising for so complex a method of deformation as rolling, and for such strong deformation, that nevertheless systematic differences are caused in the stored energy by various types of rolling (reversal or cross-rolling, respectively). This statement also applies to the results obtained for the examination of torsion copper samples. Here, stronger still than for rolling were the differences observed in the stored energy after unidirectional and cyclic torsion, respectively. At first a cylindrical sample was deformed by unidirectional torsion (i.e., with unchanged direction of rotation) up to fracture. Then the sample was cut into discs and the stored energy of each disc was measured (Fig. 4). It was observed that the stored energy
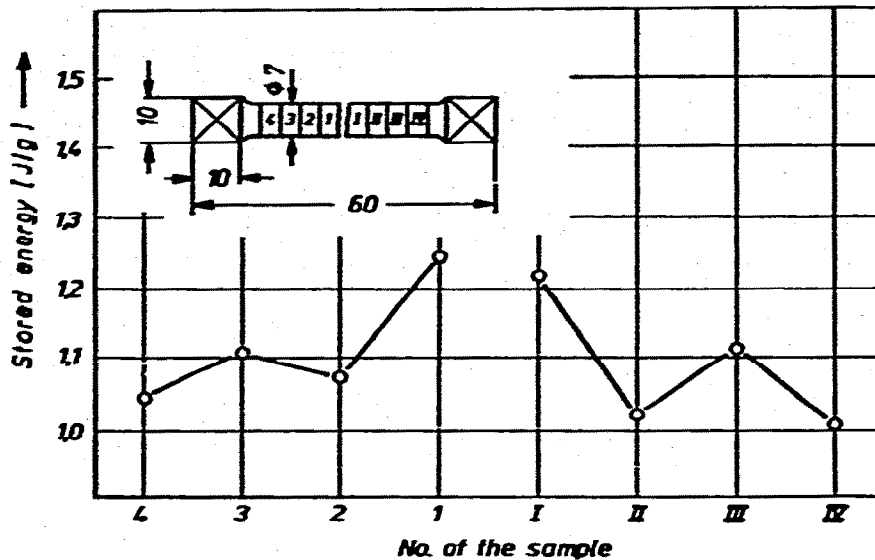
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Fig. 4. Position dependence of stored energy of a copper cylinder, fractured by unidirectional torsion. Fracture between disc No. 1 and No. I; weight of a disc about 1 g; accuracy of measurement ± 5%; linear dimensions in mm.
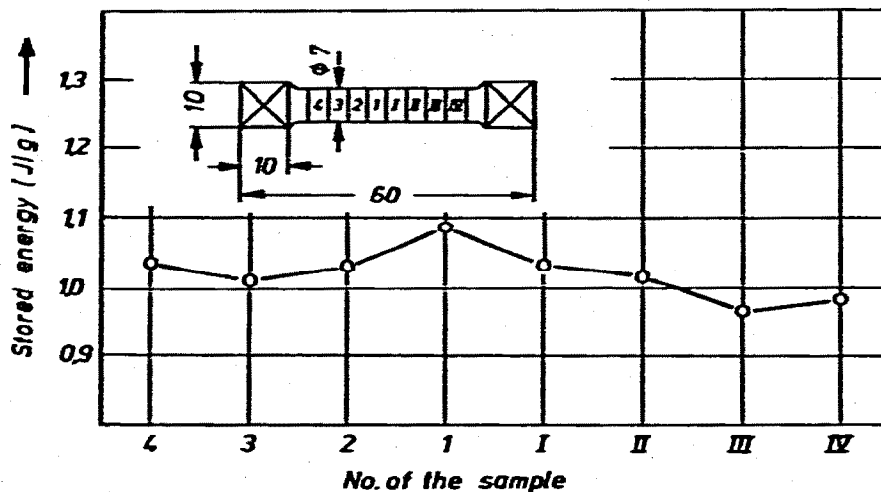

Fig. 5. Position dependence of stored energy of a copper cylinder, stressed under unidirectional torsion up to 80% of its life expectancy. Accuracy of measurement ± 5%; linear dimensions in mm.

is unevenly distributed throughout the sample length. Those samples which contain the fracture surface show a higher stored energy. However, this inhomogeneity only set in after the sample had been deformed for up to more than 80% of its life expectancy. In this phase cracks are generated at the surface which continuously decrease the effective sample cross-section, so producing increased deformation within the sample bulk, and which finally lead to fracture. Even at 80% of their life expectancy, samples showed no longitudinal inhomogeneity outside the error limit (Fig. 5). This was because here the sample cross-section which takes up the torque was not yet reduced
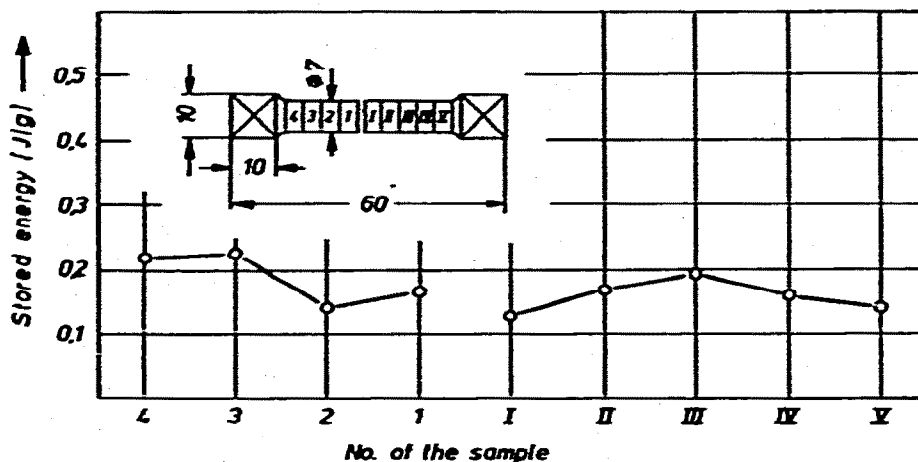
Fig. 6. Position dependence of stored energy of a copper cylinder, fractured by cyclic torsion. Angle of torsion ± 84°; fracture between disc No. 1 and No. I; accuracy of measurement ± 30%; linear dimensions in mm.

by cracks at the subsequent fracture site, and so the average degree of deformation, and with that the stored energy of the inidividual discs, remained more or less constant.

Furthermore, copper samples were examined which had been fractured by cyclic torsion (turning to and fro at a certain angle). No pronounced longitudinal inhomogeneity was found for these samples. The stored energies are very small, they amount to less than 20% of the stored energy released by the samples stressed to fracture by unidirectional torsion. Thus, for various modes of torsion the stored energies differ much more strongly than is the case for various rolling methods.

CONCLUSION

The accuracy of modern devices for quantitative DTA allows one to begin the systematic investigation of the dependence of the stored energy of cold-worked metals on the chemical composition and deformation conditions. In order to understand more clearly the effect of diverse modes of deformation on the amount of stored energy, one should have more data available on the dependence of defect structure on the mode of deformation. The same holds for the influence of foreign atoms. Since these data are lacking for higher deformed metals, to this day the measured values of the stored energy can only be related to other integral material characteristics (e.g., hardness, electrical resistivity, texture). In spite of this limitation, the stored energy plays an important role within the scope of the present concept of the deformed state and recrystallisation behaviour of metals.

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