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Heat Capacity Measurements of Pulverized Metal Hydrides between 1.5 and 15 K by means of the Cu-tabletting Method

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Abstract

The heat capacity in the temperature range 1.5 to 15 K yields a number of important informations. The examination of transition metal hydrides, however, is difficult frequently, because the samples embrittle to a fine powder with increasing hydrogen content. Therefore especially the hydrides of the lower half of the 3d transition group cannot be investigated by means of conventional techniques. In this case the copper-tabletting method is a helpful tool /1/. The finely grained hydride is mixed with high-purity copper powder and pressed to a tablet by applying a pressure of about 10 t/cm^2. The high ductility of Cu ensures mechanical stability of the tablet. The special advantage of Cu as a binder material is its high thermal conductivity which enables a fast distribution of heat within the sample. The heat capacity of Cu at low temperatures is small because of the almost vanishing electronic contribution, and its dependence on temperature can be described by a simple function. Therefore the contribution of the Cu-powder to the overall heat capacity of the specimen is small and can be substracted easily. The applicability of the method will be demonstrated by a number of examples. Informations about the low temperature phase boundaries of the V/H and the Nb/H system have been obtained, and the influence of H on the magnetic behaviour of Fe in V has been investigated. Further, a segregation of V/Ti alloys upon hydrogenation could be detected which cannot be observed neither by X-ray nor by neutron diffraction.

Introduction

Heat capacity measurements between 1.5 and 15 K yield informations about important solid state properties. In this temperature range the lowest modes only of the lattice vibrations are excited, which contribute to the heat capacity according to the third power's law of Debye. The Debye temperature may therefore be evaluated as an approximation to the elastic properties. In transition metals the electronic contribution to the heat capacity dominates the contribution of the phonons at low temperatures. In case of strong coupling between the conduction electrons and the lattice vibrations superconductivity may occur, which - as a second order phase transition - can be recognized as a jump in the heat capacity. Further contributions to the heat capacity may arise from magnetic moments.
Heat capacity measurements in the temperature range mentioned can be performed easily with bulk specimens of high thermal conductivity. Powdered materials, however, require special techniques. Such difficulties are very often encountered in the examination of transition metal hydrides, because most of the hydride forming metals become embrittled upon hydrogenation. In spite of great interest in these compounds, therefore, heat capacity measurements are rather rare. In the following a procedure will be presented for the calorimetry of powdered samples in the low temperature range. The applicability of the method will be demonstrated with some examples.

Principle of the Cu-tabletting method

Calorimetric investigations require a compact sample with high thermal conductivity and at least one even surface plain to enable good contact to the sample holder with heater and thermometer. This can be achieved also with finely grained material by compressing it to a tablet with high-purity Cu-powder /1/. For that purpose the powdered sample is mixed with Cu-powder in a volume ratio of 3:2 (sample : Cu), and then compressed with about 10 t/cm^2. Because of the high ductility of Cu the procedure yields a tablet of good consistence The grains of the sample are closely surrounded by the Cu-material, so a good thermal contact Cu → sample is guaranteed. Temperature differences in the tablet are equalized readily because of the high termal conductivity of Cu.

The heat capacity of high-purity Cu is a steady function of temperature and simply to describe. In particular, Cu does not become superconducting and shows no magnetic phase transitions. Furthermore, Cu exhibits a very low electronic contribution to the heat capacity, so that it contributes only little to the low temperature heat capacity of the specimen. It was found, however, that the heat capacity of the copper powder does not follow exactly the Cu reference equation of Osborne et al. /3/. This may be explained by the large surface of the powder connected with enhanced impurity and lattice defect concentration. The heat capacity of a Cu-tablet without sample admixture must therefore be determined separately by a calibration measurement.

Applications

The efficiency of the Cu-tabletting method may be demonstrated by means of some experimental results on pulverized Vb metals and alloys. The investigations have been performed with a calorimeter constructed by M. Mahnig and D. Ohlendorf /1/. The calorimeter enables adiabatic measurements at ambient temperatures of 1.2 K in a $^4_2$He-bath cryostat. The device is outlined in Fig. 1. The sample is fixed to the holder by means of a low temperature varnish and heated stepwise from 1.5 to 15 K. The temperatures are measured with a Ge resistance thermometer.

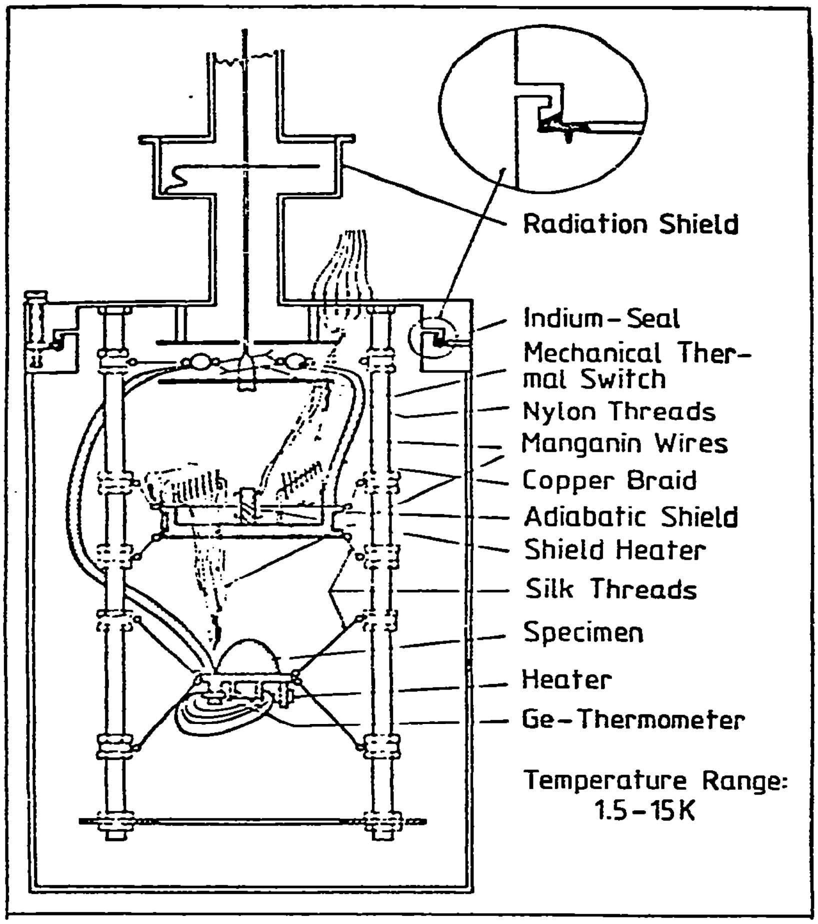

Fig. 1: Core of the Calorimeter of M. Mahnig and D. Ohlendorf /1/

Above He-bath temperature adiabatic conditions are maintained by means of a heatable adiabatic shield. A mechanic heat-switch enables rapid cooling down to the starting temperature of 1.5 K. The calorimeter was calibrated against the Cu reference equation of Osborne et al. /3/.

The first example represents the superconducting properties of V and two-phase V hydride /2/ (Fig. 2a) and the corresponding phase diagram according to Schober and Wenzl /4/ (Fig. 2b). The transition to the superconducting state is indicated by a discontinuity in the heat capacity at the transition temperature T_c. The height of the peak decrea-

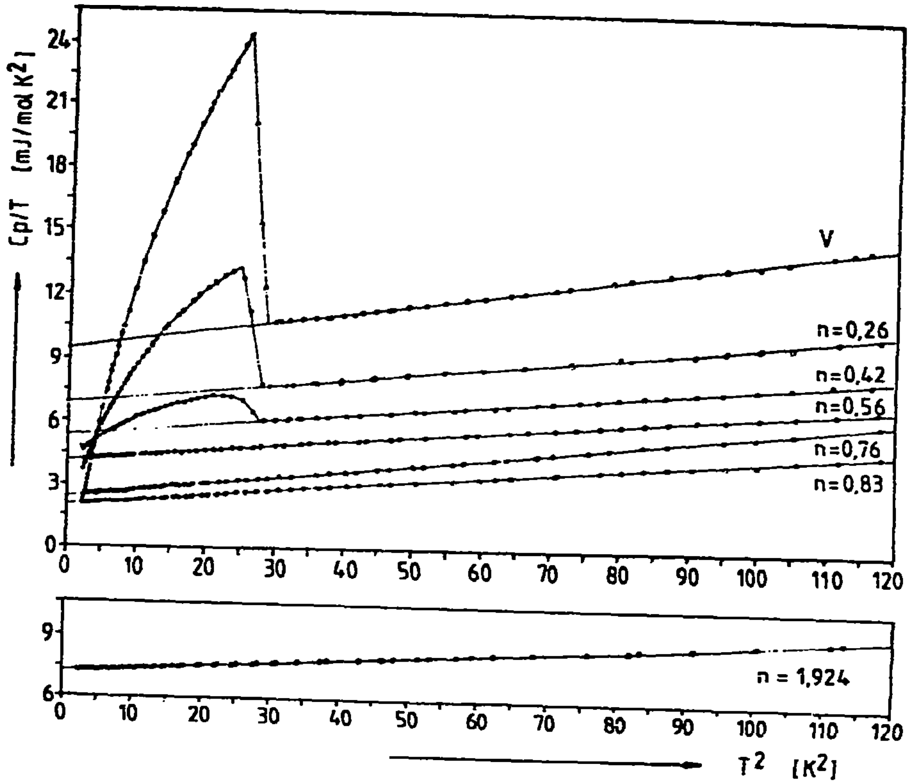

Fig. 2a: C_p/T vs T^2 of Vanadium Hydride /2/

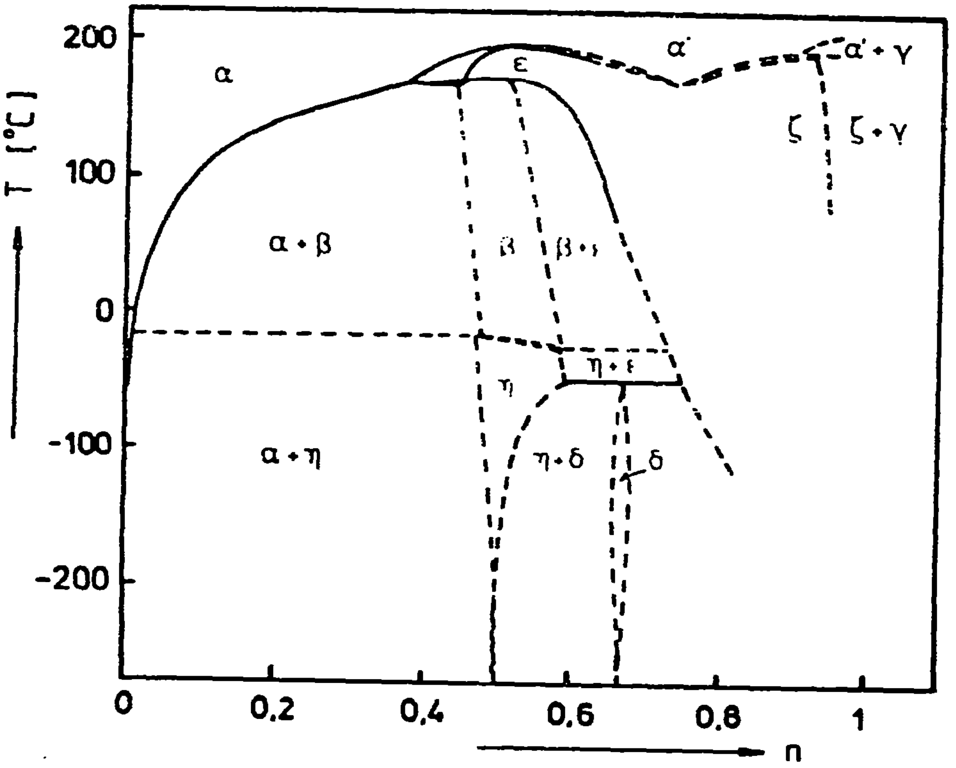

Fig. 2b: Phase Diagramm of the Vanadium Hydrogen System /4/

ses linearly with increasing H content of the sample, whereas T_c remains constant. Therefrom can be concluded that the α-hydride phase (solid solution of H in the b.c.c. V lattice; H on tetrahedral sites) exhibits the same superconducting transition temperature as pure V because of the very low hydrogen content of the α-phase at low temperatures.

The η-phase however (a speculative low-temperature modification of the monoclinic V_2H-phase; H on octahedral sites) shows no superconductivity. Within the two-phase region the height of the superconducting peak decreases corresponding to the lever rule. The results of the low-temperature heat capacity measurements therefore confirm the low-temperature phase boundaries of Schober and Wenzl /4/. It is worth mentioning that none of the hydride phases of V except the α-phase becomes superconducting above about 1.5 K. As an example Fig. 2a shows the heat capacity results of a specimen that consists almost entirely of γ-phase, VH_2 (n = 1.924 in Fig. 2a). The dihydride phase has f.c.c. structure with H on tetrahedral sites, and a transition to superconductivity might have been possible analogous to PdH which is f.c.c. as well.

Comparable results were obtained for the Nb/H system (Fig. 3) /2/. In this case the (α + ε) two-phase region ranges up to a metal to hydrogen ratio of about 0.7. Again the ε-phase (ordered orthorombic phase with the approximate composition Nb_4H_3) exhibits no superconductivity. In the Nb/H system as well only the homogeneous solution of the α-phase (that means at the temperatures in question practically the pure metal) becomes superconducting. All the other phases remain in the normal state at temperatures above 1.5 K. Again the dihydride phase is presented as an example (Fig. 3a; n = 1.93).

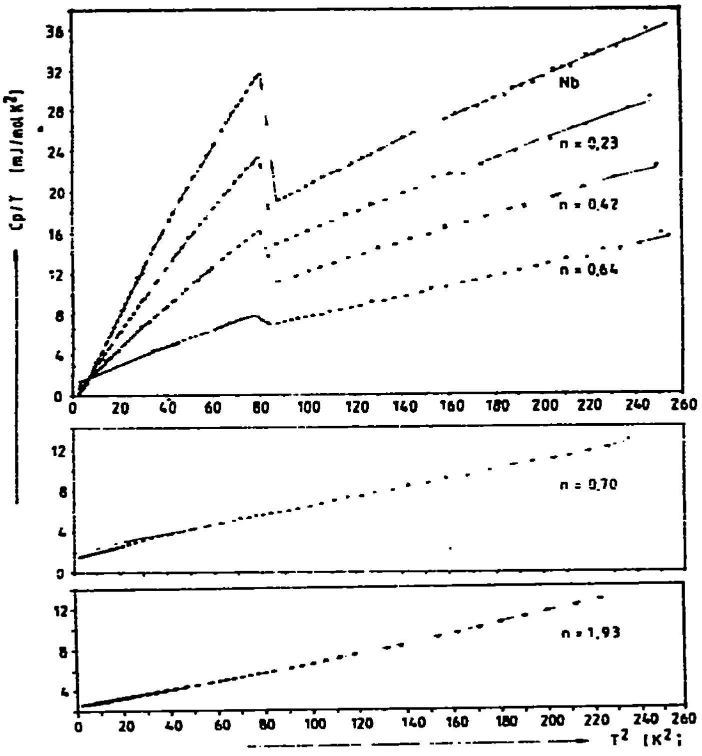

Fig. 3a: C_p/T vs T^2 of Niobium Hydride /2/

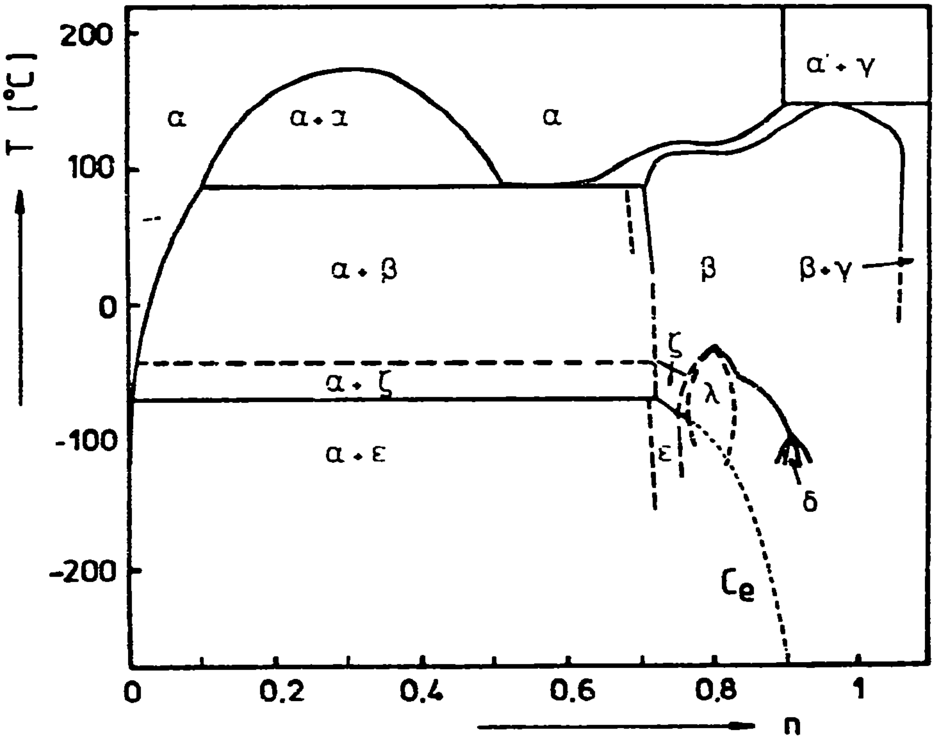

Fig. 3b: Phase Diagram of the Niobium Hydrogen System /4/

By means of the copper-tabletting method the influence of the hydrogen content on the low-temperature heat capacity of V/Fe alloys could be investigated (Fig. 4) /5/.

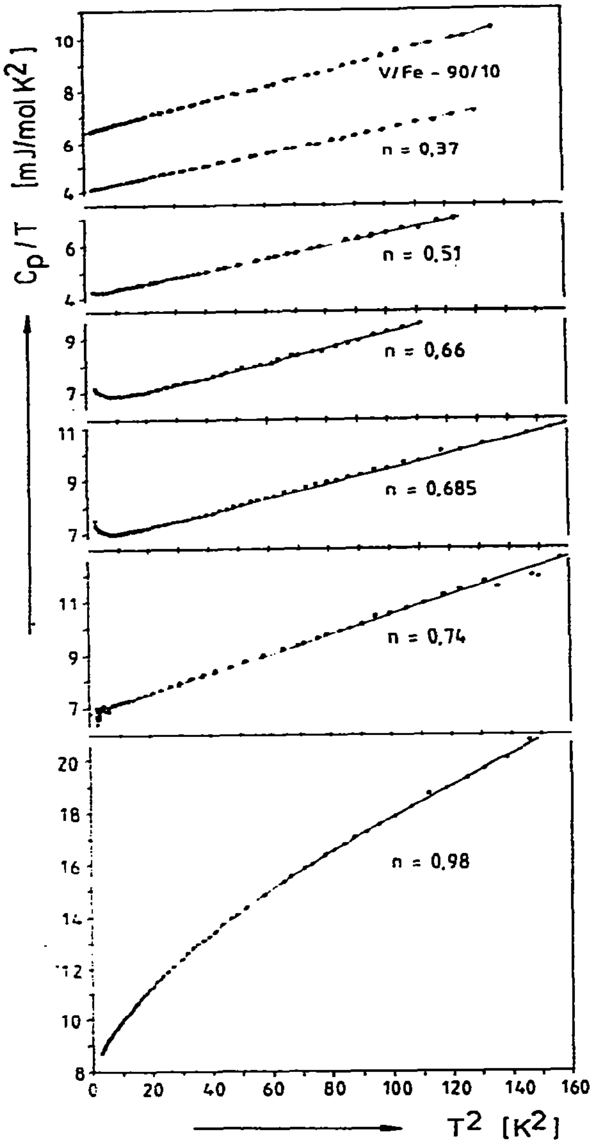

Fig. 4: C_p/T vs T^2 of Vanadium-Iron Hydride $V_{0.9}Fe_{0.1}H_n$

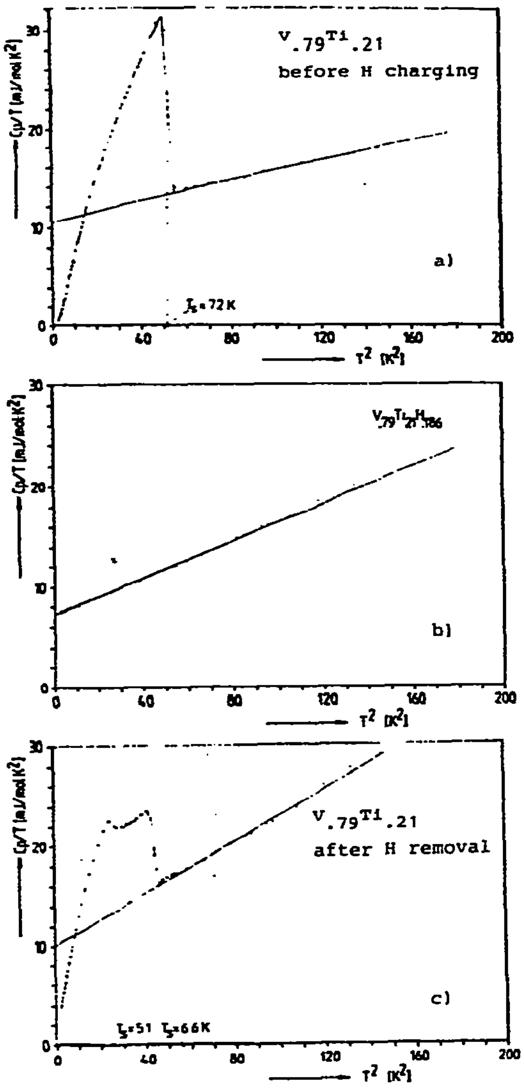

Fig. 5: C_p/T vs T^2 of Vanadium-Titanium Alloy $V_{0.79}Ti_{0.21}$ before and after H Charging resp. H Removal /8/

For special sample compositions additional magnetic contributions to the low-temperature heat capacity occur, indicated by a hyperbolic rise in the C_p/T versus T^2-plots. The effect originates in hydrogen-induced local Fe-moments which appear in a limited range of hydrogen concentration and disappear again at higher hydrogen content. If the H content is increased further, a negative deviation from the expected linear C_p/T-versus-T^2 relation is to be observed. This must be attributed to a mutual interaction of the Fe-moments.

The complicated behaviour of Fe in a V/H matrix could be confirmed and further cleared up in a study of the ^{57}Fe Moessbauer shifts /6/. The detailed and mutual influence of varying Fe and H concentrations at He temperatures is the subject of low-temperature magnetic measurements at present /7/. Of special interest is the kind of interaction between the Fe-moments mentioned before.
By means of the Cu-tabletting method evidence was found for the drastic changes of local composition and structure in the material that may occur upon hydrogenation. Especially alloys and intermetallic phases containing Ti exhibit a marked tendency to segregation brought about by the strong affinity of Ti to H. This effect is highly undesirable with regard to hydrogen-storage materials containing Ti, because it may lead to an irreversible change in the properties of such materials by continuous hydriding and dehydriding cycles. In either case the hydrogen treatment will pulverize the material, and it will remain finely grained also after removal of the hydrogen, so the Cu-tabletting method has to be applied.
An instructive example is the hydrogenation of V/Ti alloys. These systems cannot be investigated by X-ray diffraction because of the

nearly equal atomic scattering factors. Neutron diffraction is not applicable either, due to the high incoherent scattering cross-section of V. Nevertheless the segregation can be investigated by low-temperature heat capacity measurements, because the superconducting transition temperature is a function of the alloy composition. A homogeneous sample shows a sharp normal-to-superconducting transition (Fig. 5a) that disappears upon hydrogenation as is known from Vb-metal hydrides (Fig. 5b). After dehydriding at 900°C and 5×10^{-6}mbar the hydrogen-free sample exhibits different superconducting properties (Fig. 5c). This effect is strongly dependend on the hydrogen treatment the sample had been submitted.

It was found that especially elevated temperature and high hydrogen pressure favour the segregation of Ti out of the V/Ti alloy. Therefore, the properties of the sample after dehydrogenation are determined by the number of charge and discharge cycles. A "cycle" is defined as dehydriding the charged sample at 600°C and subsequent recharging under 150 bar hydrogen pressure and slow cooling down to room temperature. This treatment led to a H to metal ratio of 1.86 after 4 cycles (Fig. 5b), the H content being determined volumetrically after degassing. The influence of this procedure on the superconducting properties of the sample are to be seen in Fig. 5c. Instead of a sharp peak in the case of the uncharged sample two maxima appear which indicate different compositions within the specimen. Obviously the hydrogen treatment brought about a segregation into areas with enriched respectively reduced Ti concentration. This effect is favoured thermodynamically by the strongly negative heat of formation of Ti hydride and accelerated by the elevated temperatures and the changes in lattice spacings during the hydriding dehydriding cycles.

The results with the V/Ti alloy system prove unambigously that the segregation is a bulk effect by the hydrogen uptake. This conclusion is opposite to the statement that the observed segregations in Ti alloys should be surface effects induced by traces of oxygen in the hydrogen supply and in the vacuum system /9/.

We hope that the copper-tabletting method will help many scientists in solving their problems with pulverized materials. The examples taken from the research field "hydrogen in metals," may prove the applicability of the method.

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