

TEMPERATURE PROGRAMMED DESORPTION STUDIES ON CaNi_5 HYDRIDES

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ABSTRACT

The possibility of using temperature programmed desorption (TPD) method for evaluating the fundamental characteristics of rechargeable metal hydrides is considered. The TPD traces of $\text{CaNi}_5\text{H}_{4.8}$ give two distinct desorption peaks corresponding to the $\gamma \rightarrow \beta$ and $\beta \rightarrow \alpha$ phase transitions. The calculated activation energies of desorption are 50 and 200 KJ $(\text{mol H}_2)^{-1}$ respectively for the transitions.

INTRODUCTION

THE sorption properties of hydrogen storage compounds are usually determined by pressure-composition-temperature (P-C-T) measurements, to establish the composition and conditions of the rechargeable metal hydrides^{1,2}. There are various AB_5 -type alloys (like LaNi_5 , CaNi_5 , etc.) which have been exploited for hydrogen storage applications. The characteristics of the hydrides formed from these types of alloys have been investigated extensively³⁻⁶. The possibility of using temperature programmed desorption (TPD) method for evaluating the fundamental characteristics of the rechargeable metal hydrides has been discussed in this communication with special reference to the study of the dehydriding behaviour of CaNi_5 hydride ($\text{CaNi}_5\text{H}_{4.8}$). Although the TPD technique has been extensively used in the study of gas-solid interactions as well as in the investigation of solid state reactions, its potentialities for the characterisation of hydrogen storage systems have not been exploited so far.

EXPERIMENTAL

The CaNi_5 alloy used was obtained from Ergenics Corporation, USA as HYSTOR 201. The alloy was of 99.9% in purity and its P-C-T behaviour has been published earlier⁷.

Initially the alloy was activated at 300°C for 90 min in vacuum and then exposed to 200 torr hydrogen for 2 hr. It was then evacuated to a pressure of 10^{-6} torr and cooled to the experimental temperature 303 K. Under the experimental conditions used, two phase transitions ($\alpha \rightarrow \beta$ and $\beta \rightarrow \gamma$) were observed, which agree with the published reports². Three to four absorption-desorption cycles were carried out before the actual TPD studies were carried out.

TPD studies were carried out using a conventional static unit which could be maintained at all stages of the measurement at 1 atm, while the temperature of the alloy hydride could be increased at a programmed heating rate (B), the normal heating rates used are between 3° and 11°/min. The alloy hydride samples were obtained by hydriding the evacuated and activated alloy at room temperature and 1 atm of hydrogen. The composition of the hydride obtained by this treatment was $\text{CaNi}_5\text{H}_{4.8}$ as determined by P-C-T isotherms⁷.

RESULTS AND DISCUSSION

Typical TPD traces obtained from a hydride of composition $\text{CaNi}_5\text{H}_{4.8}$ are shown in figure 1 for the different heating rates employed. Two desorption maxima are observed. The peak around 80°C could be attributed to the $\gamma \rightarrow \beta$ phase transition and the peak around 110°C would account for the $\beta \rightarrow \alpha$ transition, which was not easily discernible in our P-C-T studies. At higher heating rates ($> 10^\circ/\text{min}$), however, this type of distinct separation between the two peaks could not be achieved and the peaks tend to overlap to give rise to a broad band of desorption. Using Van'tHoff's relationship ($\ln P$ vs $1/T$) and the enthalpy values for the phase transitions, the values of temperature deduced for these two transitions at 1 atm pressure of hydrogen are 83°C and 53°C respectively, which are lower than the observed maximum peak temperatures.

The deductions that are possible from the TPD traces are:

- (1) The total number of peaks obtained correspond to the total number of plateaus observed during hydriding upto the pressure of the experiment.
- (2) Assuming a second order desorption kinetics, the

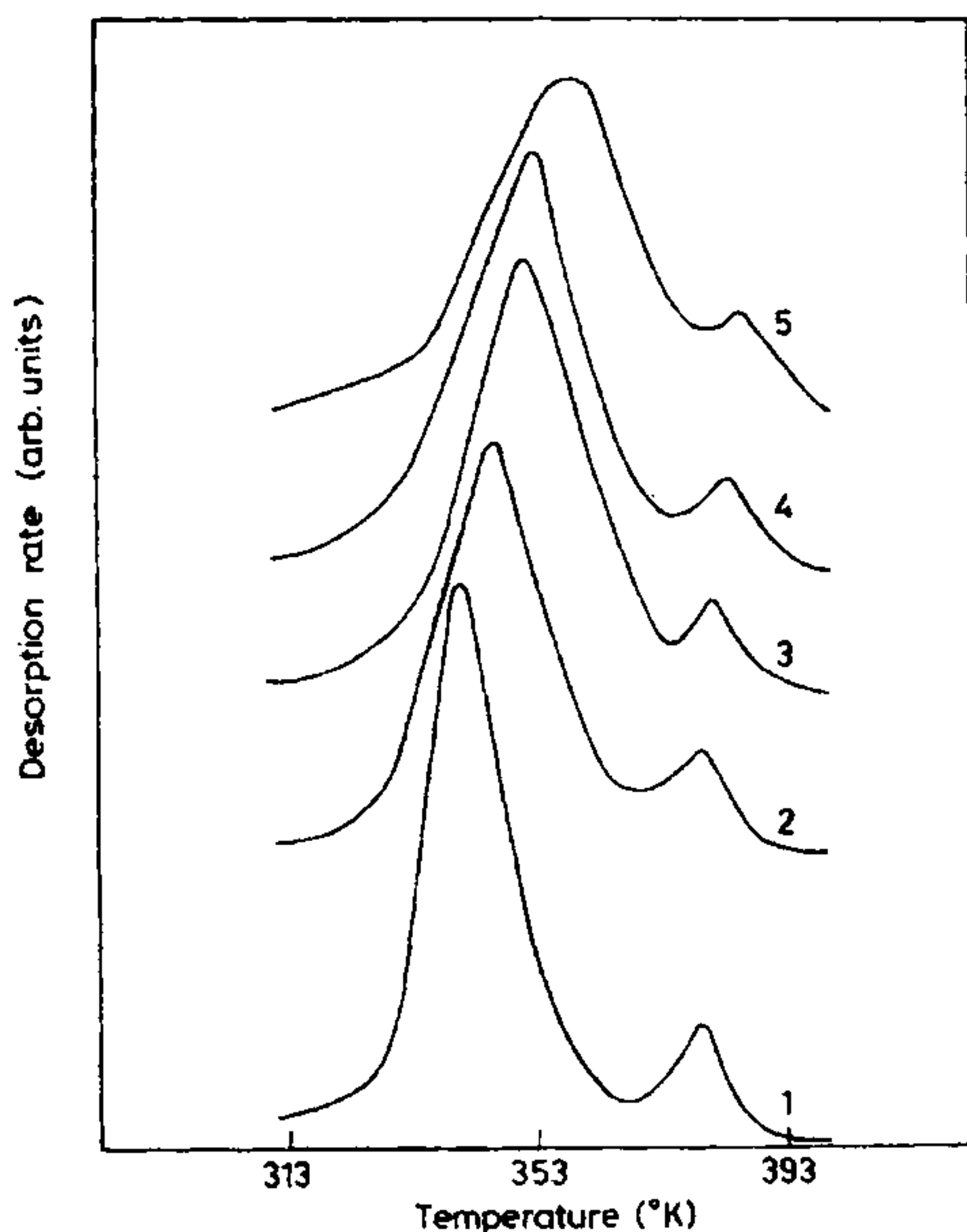


Figure 1. TPD traces for $\text{CaNi}_5\text{H}_{4.8}$ at different heating rates, B: 1, 3.5° ; 2, 4.6° ; 3, 6° ; 4, 8° ; and 5, 9° per minute.

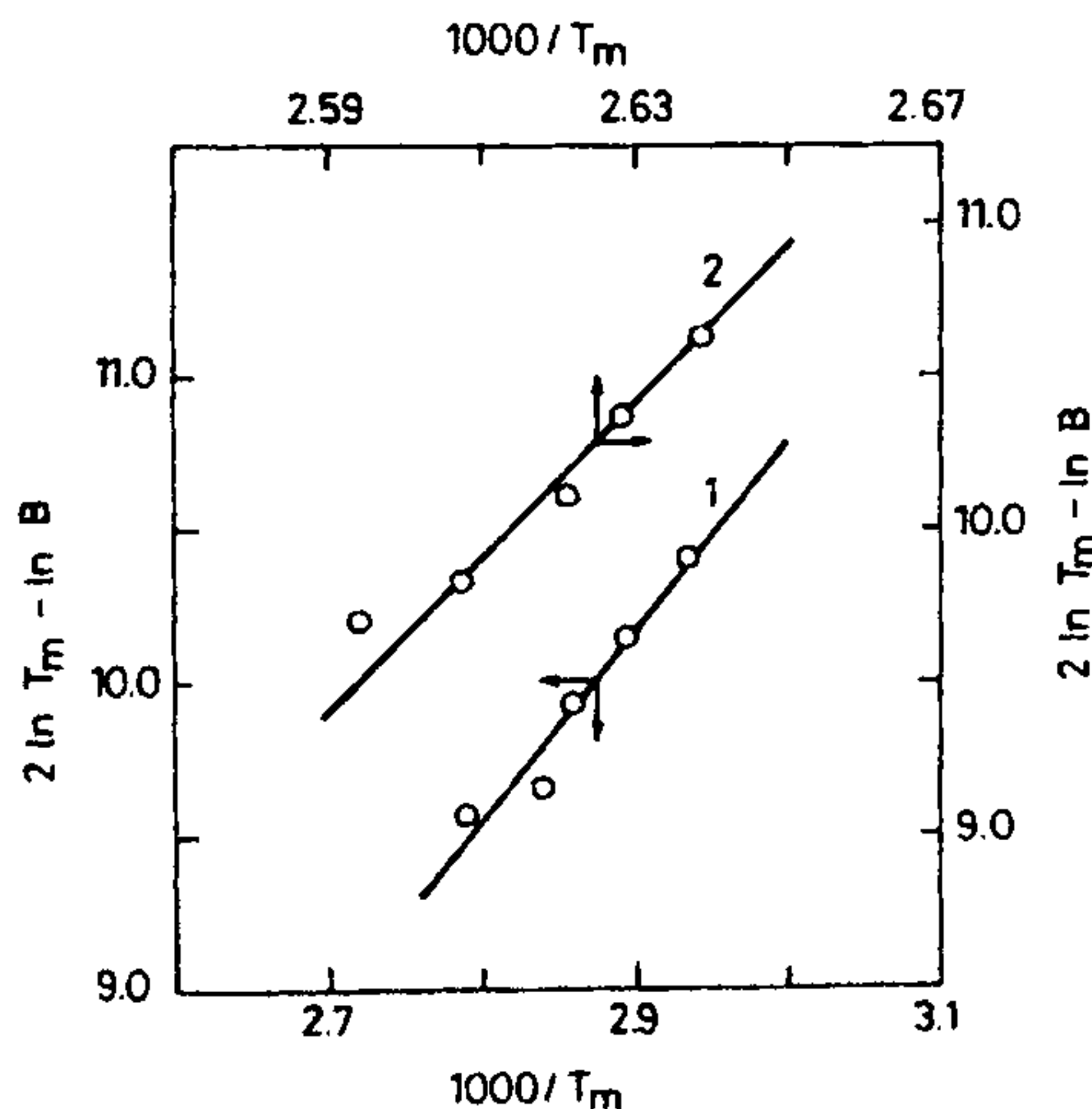


Figure 2. $2 \ln T_m - \ln B$ vs $1000/T_m$ plots for: 1, desorption from γ hydride and 2, desorption from β hydride.

data from the TPD traces were analysed. The equation for the second order desorption⁸ is

$$2 \ln T_m - \ln B = \frac{E_d}{RT_m} + \ln \frac{E_d}{2\theta_M AR}$$

where E_d is the activation energy for desorption and T_m is the desorption peak maximum temperature. The plot of $2 \ln T_m - \ln B$ vs $1/T$ is shown in figure 2 for both the peaks. The calculated value of the activation energy for desorption of hydrogen from the γ -phase is $50 \text{ KJ (mol H}_2\text{)}^{-1}$ while for β -phase the value is $200 \text{ KJ (mol H}_2\text{)}^{-1}$. The values of enthalpies of formation obtained from P-C-T isotherms⁷ are 32 and $50 \text{ KJ (mol H}_2\text{)}^{-1}$ or 34 and $43 \text{ KJ (mol H}_2\text{)}^{-1}$ respectively². (3) The intensities of the desorption peaks could perhaps be correlated to the plateau length. The plateau length in P-C-T isotherms corresponds to the extent of hydriding (or the composition of the hydride). This is only an expectation and the present data are too limited to substantiate this generalization.

The above results show that the potentialities of the TPD studies could be exploited for the study of hydrogen storage by metal alloys. We believe that this technique can replace the time-consuming conventional P-C-T measurements to evaluate the composition of the hydrides formed as well as for the determination of the activation parameters for desorption or dehydriding. However, caution should be exercised in the interpretation of the kinetic parameters deduced from the use of TPD technique, since it is essentially a non-isothermal dynamic method with its own limitations as compared to the conventional static equilibrium measurements.

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1. Goudy, A. J. and Wallingford, R. A., *J. Less-Common Met.*, 1984, **99**, 249.
2. Sandrock, G. D., Murray, J. J., Post, M. L. and Taylor, J. B., *Mater. Res. Bull.*, 1982, **17**, 887.
3. Kuijpers, F. A., *Philips Res. Rep., Suppl.*, 1973, 2.
4. Van Mal, H. H., *Philips Res. Rep., Suppl.*, 1976, 1.
5. Yagisawa, K., Yoshikawa, A. and Matsumoto, T., *J. Less-Common Met.*, 1984, **99**, 205.

6. Van Mal, H. H., Buschow, K. H. J. and Maidema, A. R., *J. Less-Common Met.*, 1974, **35**, 65.
 7. Sridhar Kumar, M. P., Viswanathan, B., Swamy,

- C. S. and Srinivasan, V., *J. Mater. Sci.*, (accepted).
 8. Tompkins, F. C., *Chemisorption of gases on metals*, Academic Press, London, 1978.

ANNOUNCEMENTS

TENTH INTERNATIONAL CONGRESS ON METALLIC CORROSION

The above International Congress will be held at Taj Coromandel, Madras, during November 7–11, 1987.

Thematic topics are as follows: (a) Corrosion Processes (Mechanistic aspects), (b) Environmental Effects (atmospheric, underground, biological, marine, liquid metal, non-aqueous, high temperature, sulphidic and vanadic, molten salts etc.), (c) Material Aspects (composition, microstructure, impurities, defects etc.), (d) Mechanical Effects (stress, fatigue, erosion, cavitation, fretting, embrittlement etc.), (e) Corrosion Control Measures (alloying, surface modi-

fication, surface coatings, inhibitors, cathodic and anodic protection, design modification etc.).

Industrial problems: Corrosion Problems in Major Industries – Fertilizer, Petroleum, Chemical, Power plants, Transport, Buildings and bridges, Food and beverages, Metallurgical, Marine.

There will be plenary lectures and panel discussions on selected topics of interest and importance.

Further details may be obtained from: Prof. Dr. K. I. Vasu, Chairman, (ICMC Organising Committee) Director, Central Electrochemical Research Institute, Karaikudi 623 006.

ELECTRICITY BY NUCLEAR POWER

Nuclear power now accounts for about 15% of world electricity production—and, in some countries, that proportion is in the range of 50–70%. Final figures for electricity production have not yet been received at the Vienna headquarters of the International Atomic Energy Agency; but some statistics are already available.

At the end of 1985, there were 374 power reactors connected to electricity supply networks in 26 countries, producing 248 577 megawatts of electrical

power. During the year, 31 reactors accounting for a total of 29 152 megawatts of electrical generating capacity (MWe) were newly connected to the grid. Construction was started on six more, with a capacity of 5180 megawatts. Two, with a combined output of only 250 megawatts generating capacity, were shut down. Notably, 1985 was the first year since the early 70s in which no contracted project was cancelled or suspended. (IAEA, PR 86/2, Vienna, Austria)