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THERMOVOLTAIC DETECTION. V. AN IMPROVED APPARATUS *

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ABSTRACT

An improved apparatus for the technique of thermovoltaic detection (TVD) is described. The apparatus is more convenient to use than previous ones due to the use of disposable metal electrodes and electrode–sample loading. The apparatus was used to study the dehydration reactions of $NiSO_4 \cdot 6H_2O$. Slower furnace heating rates greatly improved the curve peak resolution of the TVD curve.

INTRODUCTION

The technique of thermovoltaic detection (TVD) [1] consists of recording the EMF (in volts), produced by the thermal decomposition and/or thermal phase change reaction of a sample placed between two dissimilar metal electrodes, as a function of temperature. The TVD curve consists of a series of peak maxima, produced by the reaction of the sample with the metal electrodes, which are indicative of the phase changes (fusion), thermal dehydration, and thermal decomposition reactions. Numerous compounds have been investigated by this technique including metal salt hydrates [1,2]; coordination compounds [2,4]; amino acids [3]; various polymers, organic acids, coal and tobacco [2]; liquids such as water and ethanol [2], and many other substances.

In previous systems described by this laboratory [1,2], the metal electrodes (usually aluminum and platinum) had to be rigorously cleaned and abraded after each run in order to maintain a reproducible sample–metal interface. This was a tedious and time-consuming process necessitating the design and construction of a totally new apparatus employing disposable electrodes. Also, the loading or compression of the electrode–sample interface was made more reproducible. This paper describes the new apparatus and its use in obtaining the TVD curve of $NiSO_4 \cdot 6H_2O$.

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* For Part IV see C.H. Hsueh and W.W. Wendlandt, Thermochim. Acta, 84 (1985) 151.

EXPERIMENTAL

Sample holder and furnace

A schematic diagram of the sample holder and furnace assembly is shown in Fig. 1, while an overall view of the apparatus is given in Fig. 2.

Basically, the sample holder and furnace consisted of two aluminum cylinders, each 25 mm in diameter by 34 mm in length, containing the heater cartridges (33W 120VAC) and sample and electrode chamber. The cylinders were held in place by two ceramic sleeves and brackets but were permitted to slide freely in a vertical direction. Two identical heater cartridges were used, one for each of the cylinders. The sample compartment consisted of a cylindrical cavity-piston configuration in which the sample, placed in a circular ceramic sleeve, was compressed between two dissimilar thin metal disks, electrodes #1 and 2. The diameter of electrode #1 was 8.0 mm while that of electrode #2 was 11.0 mm. Compression of the electrode–sample interface was controlled by adding known weights to the weight platform. A chromel–alumel thermocouple, located in the lower cylinder, was used to detect the sample temperature and to provide temperature feedback for the temperature programmer.

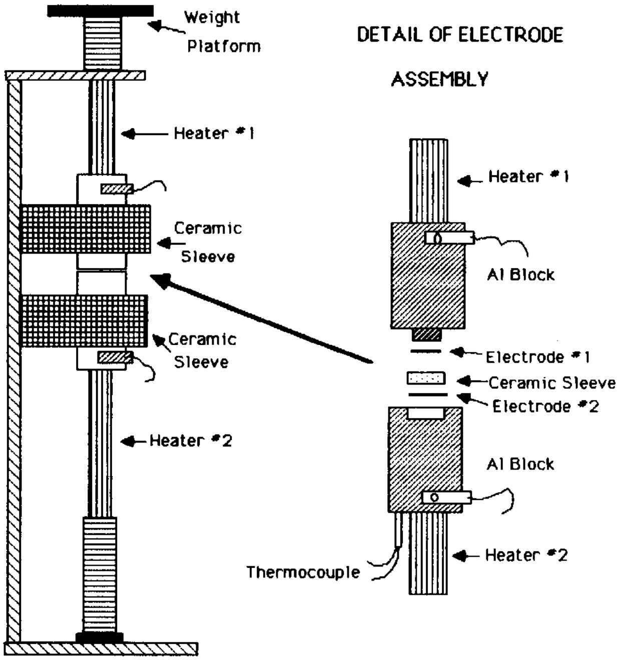

Fig. 1. Schematic diagram of sample holder and furnace assembly for TVD apparatus.

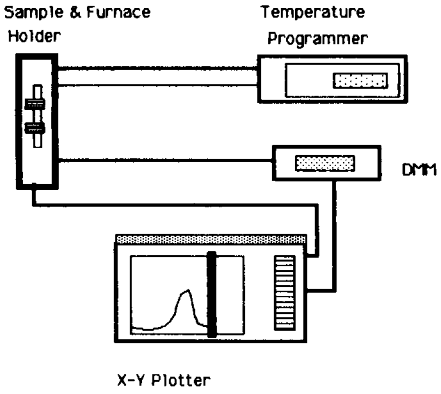

Fig. 2. Schematic diagram of TVD apparatus.

In Fig. 2, a temperature programmer (Theall Engineering Model TP-2000, Oxford, PA) was used to control the linear temperature rise of the two cylinders. The EMF output from the electrode system was led into a DMM (Keithley Model 177, Cleveland, OH). The signal output from the analog output terminals of the DMM was connected to the Y-axis of the $X-Y$ plotter (Houston Instruments Model 100, Austin, TX). The DMM permitted the monitoring of the TVD signal as well as attenuation or amplification, as needed. Sample temperature, as detected by the lower cylinder thermocouple, was recorded on the X-axis of the recorder.

Procedure

The powdered sample (5–15 mg) was placed in the ceramic sleeve, which was then assembled into the cavity of the lower cylinder. Freshly cut metal electrode disks, usually copper (#2) and aluminum (#1), were placed in contact with the sample. The upper cylinder was then lowered to make contact with electrode #1 and the sample. A suitable weight, with a mass of 340 g, was then placed on the weight platform to provide the sample–electrode loading. Different mass loadings could be employed merely by changing the weight(s). No atmosphere control was necessary due to the enclosed sample chamber.

For samples that fused during the TVD experiment, the samples were placed on thin circular Teflon or phenolic fiber washers. This arrangement prevented electrode–electrode contact and a short circuit (0 V) of the TVD signal. Also, for liquid samples, glass micro-beads were placed on electrode #2 and several drops of the sample added to the beads. As in the case above, the micro-beads prevented electrode–electrode contact.

Furnace heating rates from 0 to 20°min^{-1} were possible using the temperature programmer. For the highest resolutions of the TVD curve peaks, a slow heating rate, usually 2.5°C min^{-1}, was employed.

RESULTS AND DISCUSSION

The TVD curves of $NiSO_4 \cdot 6H_2O$ at three different heating rates are shown in Fig. 3.

The general features of the TVD curve, which are plots of EMF (V) versus temperature, show the temperature ranges at which dehydration of the metal salt hydrate occurs. As in the figure, dehydration began at about 100°C and was essentially completed at about 200°C. At the highest heating rate employed, 10.0°C min^{-1}, several peak maxima were observed in the 100–125°C temperature range followed by a shoulder peak at about 150°C. At a heating rate of 5.0°C min^{-1}, the peak area was reduced by approximately 50% with large peak maxima observed again in the 100–125°C temperature range. The shoulder peak was resolved into a small peak with a maximum at about 150–160°C. At a still slower heating rate, 2.5°C min^{-1}, the TVD curve was similar to the former except for a further reduction in peak area and a smaller peak maximum at 150–155°C. These latter curve features for the dehydration of $NiSO_4 \cdot 6H_2O$ have not been previously observed in the TVD curve [1].

The new apparatus is much easier to use than those previously described and since new electrodes are used for each run, the TVD curves were found to be more reproducible. Also, it was easier to obtain reproducible loading of the electrode–sample interface, hence increasing the reproducibility of the TVD curves.

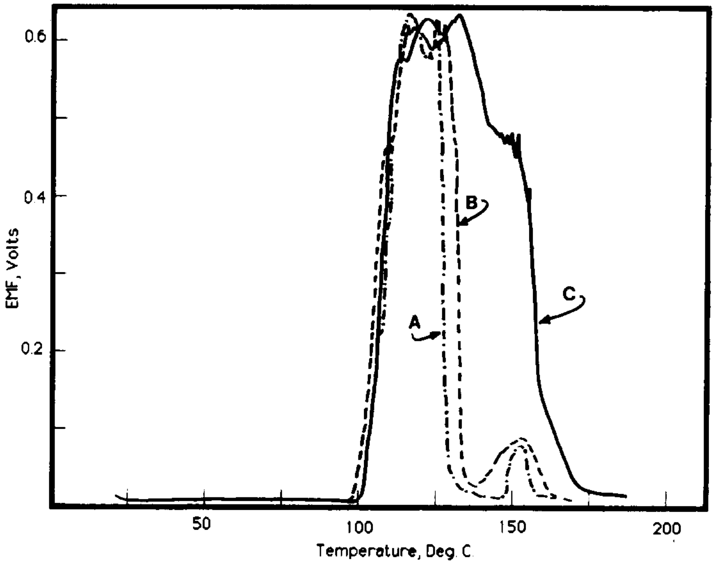

Fig. 3. TVD curves of $NiSO_4 \cdot 6H_2O$. (A) 2.5°C min^{-1}; (B) 5.0°C min^{-1}; and (C) 10.0°C min^{-1}. Mass loading of 340 g.

ACKNOWLEDGMENT

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