

A HIGH PERFORMANCE “DILATOMETER–CONDUCTIMETER” FOR GLASSES AND SOLID STATE TRANSFORMATION STUDIES

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ABSTRACT

A combined instrument in which conductivity electrodes are combined with the dilatometric measurements has been developed. For a compacted iron powder sample, results show that information may be obtained about grain contact improvement before roasting, in addition to data on transformation points.

For glassy materials in which the determination of T_g can be obtained by the dilatometric curve, it is shown that the electrical resistance curve gives more accuracy. For glassy materials for which dilatometry does not allow a determination of T_g , the electrical resistance curve provides this information.

For a copper sulfate sample, the dilatometric curve which looks like a TG curve gives much more information. In addition, the electrical resistance curve corroborates the dilatometric data and provides extra information which can be used for interpreting the dehydration process mechanism.

INTRODUCTION

For the complete characterization of the properties of a material several analytical techniques are generally required. In many instances it is very attractive to use simultaneous techniques because complementary information may then be provided, under the same experimental conditions and with gain of time. Furthermore, in some theoretical studies, such as kinetics, simultaneous data are necessary which can only be provided by a combination of techniques [1,2]. Among the thermal analysis techniques which are commonly used in Materials Science, dilatometry and conductimetry can be advantageously combined.

In earlier studies [3,4] electrical properties of materials have been reported using a commercial dilatometer simply modified by including two electrodes

in the sample holder. The apparatus developed in this work is a combined instrument in which electrodes make no contribution to the dilatometric measurements.

EXPERIMENTAL

The apparatus described operates at temperatures between liquid nitrogen and 1000°C. The dilatometer is made of vitreous silica which has a linear expansion coefficient of $0.5 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$. This value is 18 times smaller than that for alumina, so that most materials may be studied directly without any correction.

The sample (Fig. 1) lies between the rear part G of the sample holder assembly and the forward end of the silica rod which provides the mechanical junction with the electronic captor. Measurement and oven control thermocouples are located at the sample level (not shown in Fig. 1). The pushrod D contains the electrical measurement system. For very low resistances ($< 10 \ \Omega$), as in the case of metallic materials, a set of four electrodes is used. For higher resistances up to $10^{14} \ \Omega$) the standard method is employed. In this case, the pushrod and the rear part G of the sample holder both contain a platinum disc between which lies the sample. These electrodes are maintained against the sample by coil springs R and R'. A high temperature model (up to 1650°C) of this apparatus is available from Thermanalyse, 49 rue de la République, 38430 Moirans (France). Figure 2 shows the complete measurement set.

EXPERIMENTAL RESULTS

Compacted iron powder

Figures 3 and 4 show some results obtained for compacted iron powder samples under air and an atmosphere of argon, respectively. At first, the

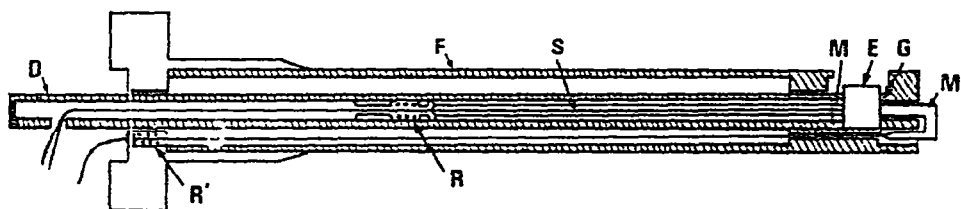


Fig. 1. Cross-section of the pushrod system and sample holder. F, Vitreous silica tube; D, vitreous silica pushrod; R, R', coil springs; S, platinum measure set; E, sample; G, rear part of sample holder; M', rear electrode; M, front electrode.

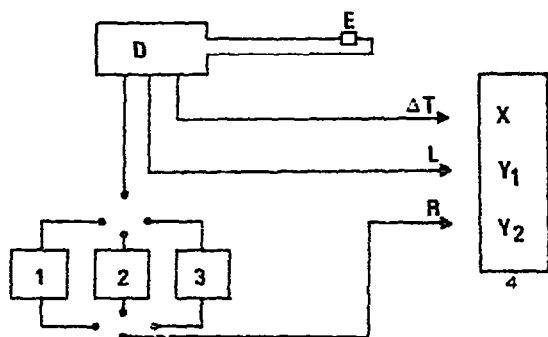


Fig. 2. The measurement set. D, dilatometer; E, sample. 1, electronic supply for low resistance measurement; 2, electronic conductimeter; 3, ultramegohmmeter; 4. X, Y_1 , Y_2 recorder

experimental curves show that the electrical resistance of the sample decreases strongly with temperature increase. Initial resistance values depend on compacting (7.3, 5.2 and 4 Ω) but reach the same value (1.6 Ω) for each sample after 250°C. It would seem that improvement of iron grain electrical contact is predominant in the first step of heating. Above 250°C, electrical resistance variation with temperature is quite conventional. Thermodilatometric curves show that for lower compacting, shrinkage due to roasting is

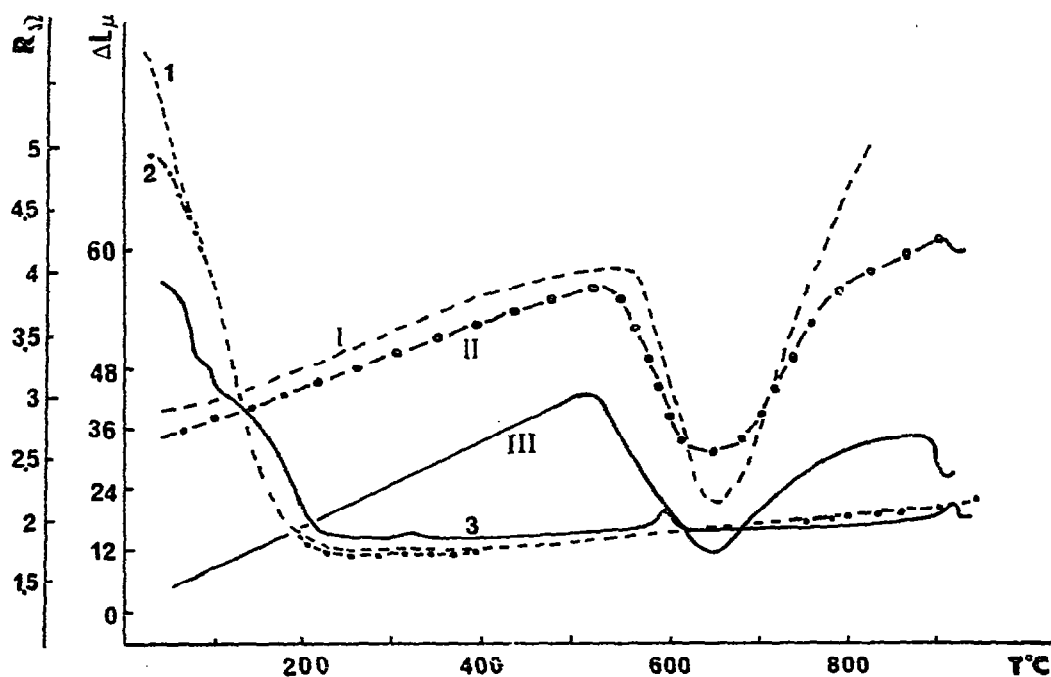


Fig. 3. Simultaneous thermodilatometric and electrical resistance curves of compacted iron powder samples. Curves I and 1, sample compacted at 750 bars; curves II and 2, sample compacted at 1500 bars; curves III and 3, sample compacted at 3000 bars. 1, 2 and 3 correspond to electrical resistance curves. Duration of compaction: 1 min; heating rate: 6 K min^{-1} ; sample size: $L = l = h = 5$ mm.

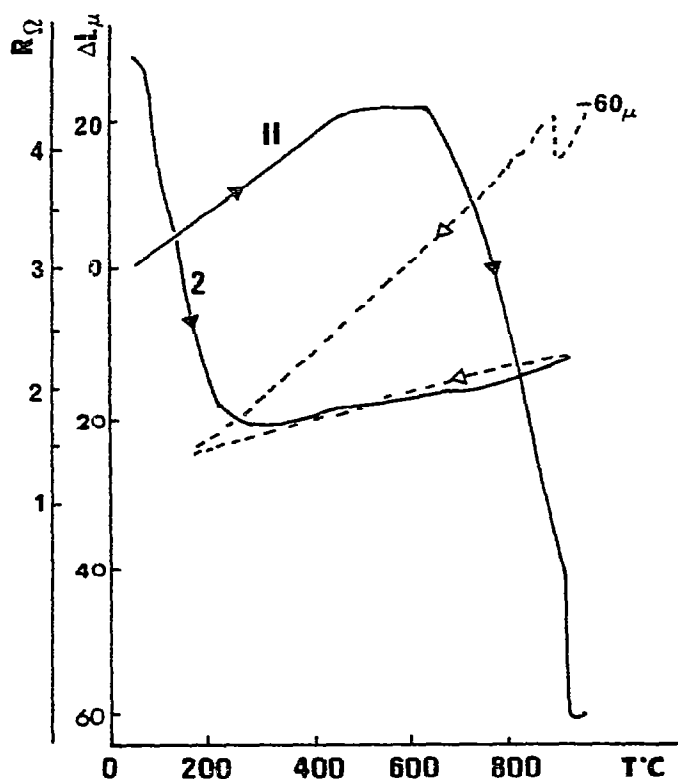


Fig. 4. Experimental curves for sample II under an atmosphere of argon. The dotted curves were obtained on cooling. Heating and cooling rate: 6 K min^{-1} .

more important and begins at higher temperatures. Above 650°C expansion due to oxidation is very important for sample I (Fig. 3) and transformation points (Curie point and α - γ transformation) are evidenced only for higher compacted samples (curves II and III).

Figure 4 shows that under an atmosphere of argon sample II electrical behavior is identical to that in air (Fig. 3) but the thermodilatometric curve exhibits a very important shrinkage and, as expected, no expansion above 650°C . It appears that under these conditions, transformation points are only evidenced on cooling (Fig. 4).

Vitreous material samples

Determination of the transformation temperature T_g for vitreous materials is currently done by dilatometry [5]. This determination is generally easy. However, for some materials the characteristic change of slope giving T_g is very difficult, if not impossible, to localize. Using electrical resistance (R) data, the T_g can be extracted with good accuracy either directly or by means of the curve $R = f \left[\frac{1}{T(\text{K})} \right]$.

Figure 5 shows experimental curves of an ionic conduction glass, an ordinary glass and an epoxy resin. As reflected by the dilatometric curves, the T_g is directly observed for the epoxy resin and the ordinary glass (curves II and III). Electrical resistance curve 1 is also given for the ionic conductor glass. As mentioned above, the slope change associated with T_g can be seen on curve 1 (Fig. 5) but an accurate localization of the relevant temperature (462°C) is only obtained through the curve $R = f[\frac{1}{T(\text{K})}]$. Note that electrical resistance curves are not given for the other samples, these having too high an electrical resistance to be represented on the same scale.

Copper sulfate $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

Powder samples (0.100 g) are compacted at 1500 bars for 1 min in order to provide 1 mm thick disc pellets. Figure 6 shows simultaneous dilatometric and electrical resistance curves. Considering $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, it is generally proposed that the first four water molecules are removed in two clearly

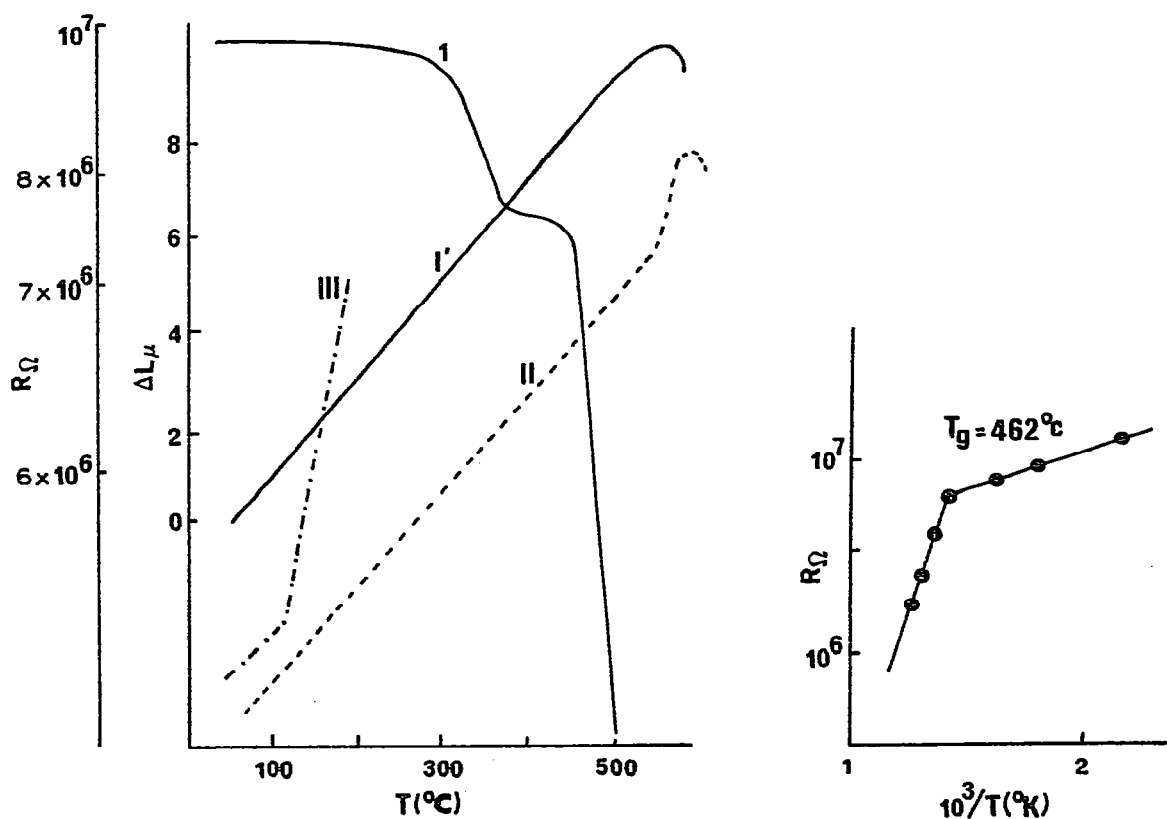


Fig. 5. Thermodilatometric curves of I', an ionic glass ($l=1$ mm); II, an ordinary glass ($l=2$ mm); III, an epoxy resin ($l=1.5$ mm). 1, Electrical resistance curve of the sample corresponding to curve I'. $R = f[\frac{1}{T(\text{K})}]$ curve for the determination of T_g .

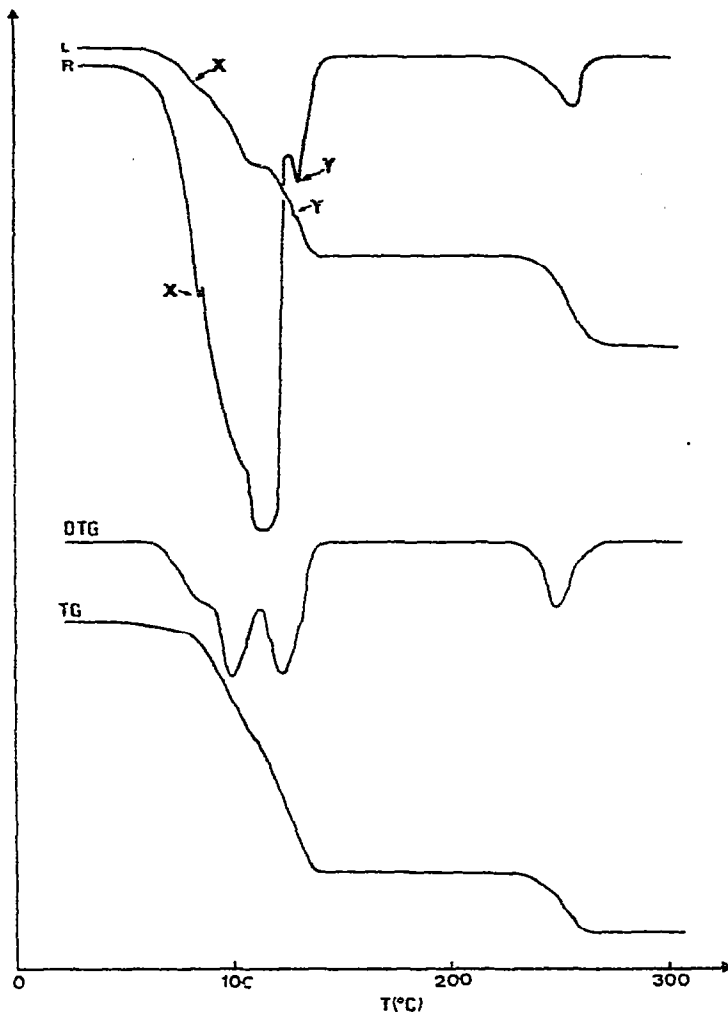
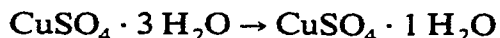


Fig. 6. Simultaneous thermodilatometric (L) and electrical resistance (R) curves of a $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ sample. DTG and TG curves of the sample are shown on the same diagram (compacting pressure 1500 bars for 1 min, heating rate: 5 K min^{-1}).

distinct steps, the removal of two molecules taking place together in each step. According to both the dilatometric and electrical resistance curves, it appears that the departure of every water molecule can be distinguished. The existence of points X and Y as revealed by dilatometric and electrical resistance curves, respectively, is corroborated by DTG experiments. In addition, the removal of the fifth "water molecule" appears clearly on the dilatometric curve as well as in TG and DTG curves, while the same is observed on the electrical resistance curve. These experimental results are not consistent with the fact that the last removed "molecule" is not a water molecule but more probably a covalent group. Such an interpretation does not fit with Todor's theory [6] which states that the "monohydrate" does not contain any water as such, but only OH groups bound in the molecule.

Furthermore, it must be noticed that generally thermodilatometric curves of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ exhibit the loss of water molecules accompanied by important shrinkage except for the dehydration reaction



for which a small expansion occurs. This phenomenon was explained on the basis of a difference in the binding energy of water molecules in the hydrate. In fact it is possible that the small expansion observed was simply due to the large size of the sample (65 mm long) where water could not leave as easily, and so promoted a small expansion of the solid.

CONCLUSION

These few examples show how much dilatometry and conductimetry are very well matched techniques for solid state transformation studies. The example of glassy materials, in which T_g can be determined from the dilatometric curve, shows that electrical resistance curves give more accuracy while, for glassy materials for which dilatometry does not allow a determination of T_g , the electrical resistance curve does. In the example of copper sulfate, the dilatometric curve which looks like a T_g curve gives much more information. In addition, the electrical resistance curve corroborates these data and also provides extra information which can be used for the interpretation of the mechanism of the dehydration process.

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