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USE OF MICROWAVES IN THERMAL ANALYSIS

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Introduction of microwaves in thermal analysis techniques may solve gradient problems and enlarge the investigation possibilities of thermal analysis. A microwave power control set up in our laboratory provides the sample with a constant and well defined heating rate. Experimental set used for DTA is described. Differential thermal curves got for some mineral products showing exothermal water departure peaks are compared to conventional DTA curves got for the same materials. Thermodilatometric curves of PVC realized with the same apparatus, under microwave and standard heating, show that transformations appear more clearly than under conventional heating. A transformation which almost is not discernible under conventional heating is clearly evidenced. As transformation temperatures under microwaves appear at lower values in DTA as in thermodilatometry, it looks probable that a part of the absorbed microwave energy enters under an other form than heat.

The stumbling-block of thermal analysis is heating. The evolution of electronics and technology has led to the use of smaller and smaller samples, so as to yield an ever lower thermal gradient. These "micromeasurements", made with microcalorimeters, micro DTA, micro TG, . . . , may not be representative of the material from which a too small sample is taken, especially in the case of composite materials. In thermodilatometry, temperature gradients cause very strong internal tensions in the sample, particularly for bad heat conductors such as ceramics, polymers and glassy materials.

In all these cases the uniform heat generation inside the sample may resolve these problems. We may therefore use quite large samples which are perfectly representative of the material.

I. Experimental set

We earlier studied the different means of measuring temperature in a microwave field and set up an apparatus giving constant heating rates [1]. In this paper, only the temperature measurement techniques used to obtain the presented experimental curves are described with the experimental set. As in the wave guide used, the $H_{(1,0)}$ mode is highly predominant, it is possible to introduce a standard thermocouple directly in the wave guide as described in a previous article [2].

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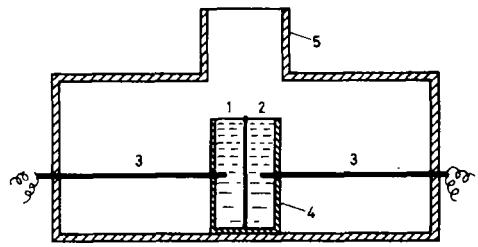

Fig. 1 Cross view of the wave guide containing the DTA sample holders and thermocouples. 1: reference, 2: sample, 3: thermocouple, 4: teflon or silica sample holder, 5: protection cylinder

The sample and the reference are placed in a 1 cm diameter cylindrical teflon or silica sample holder (Fig. 1). For convenient handling the wave guide is perforated above the sample holder and no important perturbation occurs for a cylinder is soldered around the hole. This cylinder must be at least as long as its diameter. This hole may be used to check the sample temperature with an optical pyrometer. For thermodilatometric measurements, we have set up a microwave thermodilatometer [3] which is described in a paper presented at ESTAC 3 [4].

II. DTA in microwaves

In DTA, the thermal changes in the sample are compared to an inert reference, the temperature of which will follow exactly the sample temperature till a transformation occurs. As each material has a different absorption coefficient and as this coefficient may depend strongly on temperature, it is not always possible to find a reference for a material. We have used two approaches to solve this problem.

II.1. *Dehydration of* $CaHPO_4 \cdot 2\,H_2O$

This material has a good absorption coefficient in microwaves. Temperature is measured by introducing a thermocouple into the sample as explained in section I, and information is collected by an APPLE IIe microcomputer. If the temperature due to the heating rate out of the transformation area is subtracted by the computer from the actual temperature of the sample, the plotter (Hewlett–Packard 7470 A) records the curve of Fig. 2, which shows both the standard DTA and the microwave DTA curves of a $CaHPO_4 \cdot 2\,H_2O$ sample. Water departure is clearly seen from both curves.

It appears that in microwave DTA the water departure is exothermic. This exothermic peak proves that the crystallization water leaves the sample in the form of H_2O vapor, which has an absorption coefficient about 1000 times higher than that of the sample. If the crystallization water had left the sample in radical form, this peak would have been endothermic. The same fact is observed in the thermal curves of $CaSO_4 \cdot 2\,H_2O$.

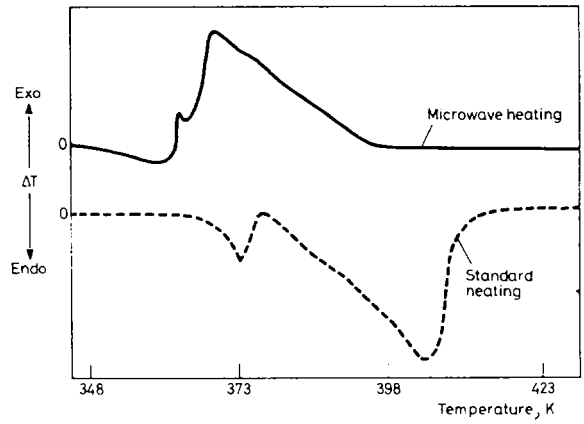

Fig. 2 Standard DTA and microwave DTA curves of $CaHPO_4 \cdot 2\,H_2O$. Heating rate: 5 deg min^{-1}

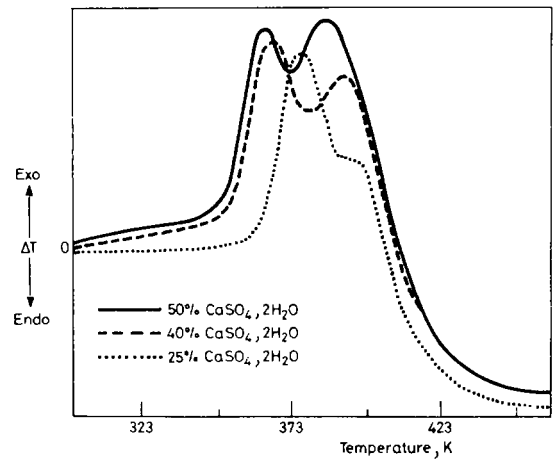

Fig. 3 Microwave DTA curves of pure gypsum mixed with different amounts of TiO_2

II.2. *Dehydration of* $CaSO_4 \cdot 2\,H_2O$

For materials having a very low absorption corfficient in microwaves, it is possible to mix them homogeneously with an inert powder having a good absorption coefficient, Al_2O_3 for instance [5]. The reference material is used for the DTA and for temperature regulation. Figure 3 shows the DTA curves given by a sample of $CaSO_4 \cdot 2\,H_2O$ mixed with different amounts of TiO_2. The exothermic peak proves that the water is released in vapor form and, as expected, the maxima of the peaks are displaced to higher temperatures at the higher heating rates obtained by increasing the TiO_2 content of the sample.

III. Thermodilatometry in microwaves

The use of microwaves is very valuable for thermodilatometry because of the mechanical effects due to temperature gradients. Polymers are generally bad heat conductors and it is difficult to determine precisely their transformation temperature.

Figure 4 shows the thermal curves given by a sample of polyvinyl chloride with conventional and microwave heating, both curves were recorded with the same apparatus.

The curves show that in microwaves transformations appear at lower temperatures, and much more clearly. Some transformations which are almost absent on standard heating are very well evidenced by microwaves (see point *A* in the curves). Both curves were recorded at the same heating rate (3.5 deg min^{-1}).

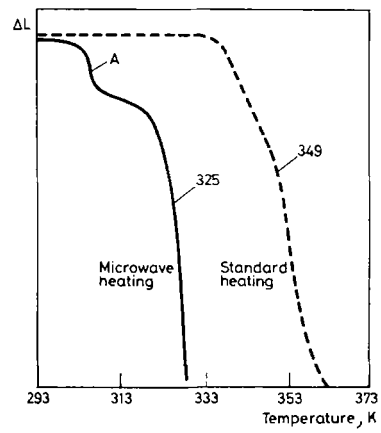

Fig. 4 Thermodilatometric curves given by a PVC sample with conventional and microwave heating. Heating rate: 3.5 deg min^{-1}. Temperature measured and controlled by a thermocouple and an optical pyrometer

Conclusions

The use of microwaves is very valuable in thermal analysis. In DTA, the example of pure gypsum shows that it is possible to study even weakly absorbing materials; it shows that water departure temperature peaks are displaced to higher temperature values as in standard heating, when heating rate increases. The example of $CaHPO_4 \cdot 2\,H_2O$ shows that the DTA curves provide evidence of the form in which water leaves the sample. The example in thermodilatometry shows that a transformation which almost is not discernible under conventional heating is clearly evidenced under microwave heating; transformations appear generally more clearly and at lower temperatures than under conventional heating. As transformation temperatures under

microwaves appear at lower values in DTA as in thermodilatometry, it looks probable that a part of the absorbed microwave energy enters under an other form than heat. An interpretation taking into account activation energies is now engaged at the present time.

References

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Zusammenfassung – Die Einführung von Mikrowellen in thermische Analysentechniken kann Gradientenprobleme lösen und die Aussagemöglichkeiten der thermischen Analyse vergrößern. Ein in unserem Laboratorium eingesetzter Mikrowellengenerator ermöglicht die Aufheizung der Probe mit konstanter und gut definierter Geschwindigkeit. Eine zur DTA benutzte Versuchsanordnung wird beschrieben. Die für einige mineralische Substanzen mit exothermen Wasserangabepeak erhaltenen DTA-Kurven werden mit den konventionellen DTA-Kurven der gleichen Materialien verglichen. In mit der gleichen Apparatur aufgenommen thermodilatometrischen Kurven von PVC sind bei Anwendung der Mikrowellenheizung Umwandlungen klarer zu erkennen als bei der herkömmlichen Verfahrensweise. Eine bei konventionellen Aufheizen meist nicht erkennbare Umwandlung wird klar nachgewiesen. Da bei Mikrowellenheizung die Umwandlungstemperatur bei DTA-Versuchen niedriger als bei thermodilatometrischen Experimenten liegen, erscheint es als wahrscheinlich, daß ein Teil der absorbierten Mikrowellenenergie in einer anderen Form als in der von Wärme aufgenommen wird.

Резюме – Введение микроволноводой в термические методы анализа решает проблему градиентов и увеличивает возможности термического анализа. Микроволновая силовая установка, изготовленная в лаборатории авторов, обеспечивает нагрев образца с постоянной и хорошю определяемой скоростью нагрева. Описана экспериментальная установка для использования ее в ДТА. Дифференциальные термические кривые, полученные для некоторых минералов, показывающих экзотермические пики выделяющейся воды, сопоставлены с обычными кривыми ДТА, полученных для этих минералов. Термодипатометрические кривые для ПВХ, полученные на этой же установке при микровольновом и стандартном нагревах, показали более четкое проявление превращений по сравнению с обичным нагревом. Поскольку при микроволновом нагреве температуры превращения наблюдаются при более низких значениях как в ДТА так и в термодилатометрии, поэтому возможно, что часть поглощенной микроволновой энергии, кроме нагрева, расходуется и на другие формы.