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Short Communication

FURTHER THOUGHTS ON TEMPERATURE OSCILLATION IN THERMAL ANALYSIS

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Abstract

Temperature oscillation has been used in various applications of thermal analysis, such as relaxation, non-stoichiometry and chemical reactions. However, there are common essential points in these applications, and these are discussed in this short communication for further understanding significance of the temperature oscillation in thermal analysis.

Keywords: chemical reaction, DSC, kinetics, non-stoichiometry, relaxation, repeated temperature scanning, temperature modulation, temperature oscillations, TG, thermal analysis

Since temperature modulated differential scanning calorimetry (tm-DSC) was set forth by Reading and his co-workers [1] in 1993, temperature oscillation has drawn much attention in the field of thermal analysis, and this new mode of temperature control was diffused into other techniques. For instance, temperature oscillation was introduced into thermogravimetry (tm-TG) [2]. Stimulated by these researches, the present author also proposed a method by repeated temperature scanning, and multiple equivalent isothermal curves were derived from a single TG curve [3]. Temperature oscillation was also applied to non-stoichiometry of high temperature oxide superconducting material and Lissajous figures derived by this method are clearly shown to be a very powerful tool to illustrate nature of non-stoichiometry [4]. Thus, including our papers many papers on temperature oscillation have hitherto been published. It seems worthy to elucidate significance of temperature oscillation methods in their essence.

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Two fundamental concepts are existing; they are temperature modulation and repeated temperature scanning. In the temperature modulation, the amplitude of the temperature oscillation is generally small, and response of the sample to this perturbation by temperature oscillation is observed. The observed responses can be the heat flow (enthalpy), the sample mass etc. The responses are usually analyzed by Fourier analysis, and the responses are separated into in-phase responses and out-of-phase responses, though their physical meanings are discussed from various points of view. On the other hand, in the repeated temperature scanning, the sample is heated and cooled in a large temperature range for observing the sample behavior by this temperature scanning. The amplitude of the temperature oscillation is in a range from 50 and 200°C. Till now only observed is the sample mass change. By extracting data of the mass and the mass change rate at a given temperature, we can get a relation between the mass and the mass change rate at this temperature, and it is equivalent to that obtained by an isothermal run. Thus we can get equivalent isothermal curves at multiple different temperatures by a single run. Another application of this method is observation of non-stoichiometry, in which we get a Lissajous figure by plotting the mass *vs.* the temperature [4].

However, the essential point in these methods is the same. When the property being observed in the thermal analysis is dependent only on the temperature, we do not observe out-of-phase component in the response and, we get a single curve in the plot of the property *vs.* the temperature (the Lissajous figure), provided that detectable time lag does not exist in the measurement [5]. For instance when detectable difference exists between the sample temperature and the temperature of its sensor, apparent difference is observed in the sample behavior between the heating mode and the cooling mode. However, when such difference is not detectable, the single curve in the Lissajous figure is independent on temperature control modes, e.g., frequency.

The sample behavior becomes different, when the property is dependent on the temperature and also on the time because of kinetic effect, such as in relaxation. In this case it takes a certain time for the sample to reach to stable state or equilibrium, and due to this kinetic effect, we get an ellipsoid-like cyclic curve in a Lissajous figure and we also observe the out-of-phase response. It can also be said that the out-of-phase response and the ellipsoid-like cyclic curve in the Lissajous figure are observed when the sample property is dependent on its previous thermal history (namely hysteresis). One example is glass transition of polymers observed by tm-DSC [6], and another example is non-stoichiometry observed by repeated temperature scanning [4]. In the latter case the large amplitude of temperature oscillation is preferable for detecting the effect by enlarging the mass change.

When we observe these phenomena at very low frequency (or at very low rate of heating and cooling), we do not observe the out-of-phase response (nor the ellipsoid-like cyclic curve but a single curve) because enough time is given to the sample to reach to the stable state, and what we are observing is the temperature change of the sample property in the stable state. In contrast with this, at a very high frequency or at a very high rate of heating and cooling, the change in the sample property cannot be observed, because time to change is not given to the sample. At a certain intermediate frequency, in which the rate to reach to the stable state is comparable to the frequency or the rate of heating and cooling, enough time is not given to the sample, so that the sample follows the stable state but with detectable time lag. Thus, we observe the large detectable effect or the large detectable out-of-phase response. This frequency dependence is very important to get insight into the sample behavior. For instance, it was elucidated that in $YBa_2Cu_3O_{7-\delta}$ three types of oxygen at three different crystalline sites are involved in the non-stoichiometry [4]. It was found because their kinetics and hence their frequency dependence are different from each other. Therefore, we observed three different behaviors in the frequency dependence.

To understand chemical reactions under the temperature oscillation, a similar but somewhat different viewpoint is needed. For simple chemical reactions [3, 7] in which only a single elementary process is involved, the rate of chemical reaction is dependent only on the temperature and the conversion. Thus we can get a single equivalent isothermal curve at a given temperature, and we can also estimate the activation energy from the response in the reaction rate, as done by tm-TG [2]. Kinetics of these reactions can be expressed as a single curved surface in three-dimensional space of the temperature, the conversion and the rate of conversion. This is corresponding to the above single curve in the Lissajous figure, and it is not dependent on the temperature controlling modes, such as constant rate heating, sample controlled thermal analysis, temperature modulation etc. In chemical reaction research, observation of this type is done by moving on this surface from zero conversion to completion. The trajectory is determined by the sample thermal history or the temperature control mode. Furthermore, this curved surface can be expressed as a single line in the plots of the conversion *vs.* the generalized time (or the reduced time) [8, 9]. The generalized rate of conversion *vs.* the generalized time and also the generalized rate of conversion *vs.* the conversion are the other expressions [8–10]. The generalized time is time integration of temperature dependence, so that it expresses combined effect of the time and the temperature.

Diffusion can also be treated in the same way, because the concentration profile in the sample is dependent only on the generalized time and the volatilization rate is dependent only on the temperature and the concentration profile [11].

For the other chemical reactions in which involved elementary processes are multiple processes of different temperature dependence or different activation energy, the rate of chemical reaction depends on the temperature and the conversion, and it is also dependent on the sample previous thermal history [12]. Thus, we cannot get an equivalent isothermal curve of the rate of chemical reaction versus the conversion, but the rate in heating mode is different from that in cooling mode. Thus the kinetics of these reactions under temperature oscillation cannot be expressed as a single curved surface in the above-mentioned three-dimensional space but only as a trajectory, and the trajectory depends on the rate of heating and cooling and also on the maximum and minimum temperatures. This complexity is the same as the above frequency dependence, and in general it cannot be simplified by introducing the generalized time and the generalized rate of conversion, because multiple generalized times are necessary to describe the reaction and the mutual relations among these generalized times are complicated [13]. In this sense temperature oscillation is a powerful tool to distinguish whether the reaction under observation is a simple reaction or not.

Crystallization is a special case in which two processes are involved, i.e., nucleation and growth, but non-isothermal kinetics was derived before [14, 15]. It is possible to introduce a single concept for simplifying the overall crystallization process, and this concept is complicated integral of two generalized time of the above two processes [8]. However, it cannot be treated easily and it is practically not useful because of complexity. Plots of crystallization rate *vs.* conversion (degree of crystallinity) might be interesting to observe the nature of the crystallization. Exception is a case that nuclei are pre-existing and do not form during the growth process. In this exceptional case the process is simple; the single generalized time can be introduced and it is useful [15]. Therefore, the above-mentioned simple relations hold.

In the above sense, an interesting example is depolymerization or unzipping producing monomer. One example is thermal decomposition of poly(methyl methacrylate) in inert atmosphere [16]. In this reaction radical is formed by some elementary processes at weak links, at polymer chain ends or at random points in the main chain, and the radical is annihilated by radical recombination or disproportionation. The radical concentration reaches to a constant in steady state, where the rate of radical annihilation becomes equal to the rate of radical formation. Moreover, the constant radical concentration in the steady state is dependent on the temperature. Thus this decomposition proceeds by a first order reaction, because the radical amount in the steady state is proportional to the sample mass and it is also proportional to the mass loss rate. The steady state is a stable state in the sense that there is restoring force to the steady state, and from the sense of kinetics its role is the same as equilibration. This effect of time for reaching to the steady state on thermoanalytical observation was considered before [10], but at that time there was no method to investigate this effect.

Supposing that time to reach to the steady state is comparable to the frequency or the rate of heating and cooling in the above depolymerization, response of the radical concentration to the temperature oscillation would be just the same as the above-mentioned response of enthalpy or mass to the temperature oscillation. Thus the out-of-phase response would be observed and the radical concentration would change along an ellipsoid-like cycle in a Lissajous figure. Therefore, we would observe that the curve of the mass loss rate *vs.* the mass in cooling would be different from that in heating, even though both are first order reactions. This difference stems from time delay to reach to the steady state, and the difference would be frequency dependent. However, this has not yet been observed, and the suitable rate of heating and cooling for observation might be very high.

The concept and theoretical considerations of the sample behavior responding to the temperature oscillation is, thus, quite similar to the sample behavior responding to other oscillation, such as polarization of dielectrics responding to alternating electric field and deformation of viscoelastic materials responding to dynamic mechanical stress. These concept and theoretical considerations would also be applicable to other thermal analysis, such as thermomechanical analysis (TMA). In this new technique of TMA, dimension would be measured under temperature oscillation. The essential points are stable state or equilibrium, approach to the stable state or equilibration by restoring force and the previous thermal history. For chemical reactions a similar method has also been used in electrochemistry. That is cyclic voltammetry, in which electric current by electrode reaction is plotted *vs.* applied voltage, while the voltage is repeatedly scanned in a wide range. Observation of effect of cyclic light irradiation in photochemical reaction study is also the same. When we observe hydration and dehydration process under constant water partial pressure by wide range temperature oscillation, we would get a similar cyclic curve of the mass or the mass change rate *vs.* the temperature, and the curve would be frequency dependent. Suggestive experimental results for possibility of this type of observation were described in a recent paper [17]. Narrow range oscillation within partial dehydration might give another view, and it would be similar to the behavior of the high temperature oxide superconducting material.

Thus the temperature oscillation method can distinguish whether the process we are observing is dependent on the sample previous thermal history or not. This point is the essential nature of the process. When equilibration or steady state is involved and it is temperature dependent, cyclic change in a certain quantity would be observed. Thus its kinetics can be elucidated by observing frequency dependence, while these points cannot be elucidated by the other methods. Therefore, temperature oscillation is very useful, and it should be more intensively studied.

To describe and to consider the oscillating behavior, Euler equation and determination of unknown parameters by assuming steady state oscillation are very powerful mathematical tools [4, 5]. The methods for analyzing the results, such as Fourier analysis and Lissajous figures, would also be helpful to get insight into the observed processes. However, it should be noted that these mathematical methods and Fourier analysis are based on linearity of the process. It should also be noted that decrease in the amplitude and shift of the phase angle occurs inevitably during the temperature wave propagation in the instrument and into the sample. They cause errors, so that thin specimens are preferable, and when specimens of low thermal diffusivity, such as polymers and powders, are observed, these effects should be taken into accounts [5]. Thermal contact between the specimen and the instrument may have also large influence on the results [5].

References

1 M. Reading, E. Elliot and V. L. Hill, J. Thermal Anal., 40 (1993) 949;
P. S. Gill, S. R. Sauerbrumn and M. Reading, J. Thermal Anal., 40 (1993) 931.
2 R. L. Blaine and B. K. Hahn, J. Therm. Anal. Cal., 54 (1998) 695.
3 T. Ozawa, Thermochim. Acta, 356 (2000) 173.
4 T. Ozawa, J. Therm. Anal. Cal., 72 (2003) 337.
5 For example, K. Kanari and T. Ozawa, Thermochim. Acta, 399 (2002) 189.
6 B. Wunderlich, A. Boller, I. Okazaki and S. Kreitmeier, Thermochim. Acta, 282/283 (1996) 143;
A. Boller, I. Okazaki and B. Wunderlich, Thermochim. Acta, 284 (1996) 1.
7 R. Sarra, J. Sempere and R. Nomen, Thermochim. Acta, 316 (1998) 37.
8 T. Ozawa, Bull. Chem. Soc. Jpn., 38 (1965) 1881.

9 T. Ozawa, Thermochim. Acta, 100 (1986) 109.
10 T. Ozawa, J. Thermal Anal., 2 (1970) 301.
11 T. Ozawa, J. Thermal Anal., 6 (1974) 401.
12 T. Ozawa, J. Thermal Anal., 39 (1993) 1117.
13 For example, T. Ozawa, J. Therm. Anal. Cal., 60 (2000) 887.
14 T. Ozawa, Polymer, 12 (1970) 150.
15 T. Ozawa, Bull. Chem. Soc. Jpn., 57 (1983) 639.
16 For example, T. Ozawa, M. Kanazashi and R. Sakamoto, Thermochim. Acta, 109 (1986) 285.
17 H. Takahashi, C. Yamaguchi and Y. Nishiyama, Netsu Sokutei, 30 (2003) 85.