

APPLICATION OF SCTA METHODS FOR KINETIC ANALYSIS OF SOLID STATE REACTIONS AND SYNTHESIS OF MATERIALS

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The advantages of the sample controlled thermal analysis (SCTA) for performing the kinetic analysis of solid state reaction as compared with conventional non-isothermal methods order, diffusion and formation and growth of nuclei (Avrami–Erofeev) controlled reactions have been analysed. It has been shown that the shape of the α - T plots recorded under a strictly constant reaction rate (CRTA) is characteristic of the kinetic model obeyed by the reaction. Thus, it would be possible to discern among boundary n just from the inspection of the shape of a single CRTA plot. The α vs. T plots of ‘ n order’ reactions have a concave shape while the α - T plots corresponding to diffusion controlled processes are sigmoid shaped with an inflection point at a particular value of α characteristic of every particular diffusion model (D_2 , D_3 or D_4). The α - T profiles of reactions fitting the Avrami–Erofeev kinetic model start with a rise in temperature until reaching the preset reaction rate. This step is immediately followed by a temperature fall (until reaching a determined value of the reacted fraction (α_n) that is depending on the value of the n coefficient in the Avrami–Erofeev kinetic equation) and again a temperature rise once the corresponding α_n value is attained. It has been shown that the value of α_n exactly agree with the value of the reacted fraction at which the reaction rate reach a maximum under isothermal conditions. This fact suggests that the part of the α - T profile in which the curve back on itself would correspond to the acceleratory period in which the total surface area of the growing nuclei would be increasing leading to an acceleration of the reaction that would be offset by a diminution of the temperature. The later rising temperature stage would correspond to the decay period in which the growing nuclei overlap among themselves with the corresponding decrease of the interface reaction area that would lead to a decrease of the reaction rate that must be compensated by a rise in temperature in order to maintain the reaction rate constant.

A comparison of (CRTA) and stepwise thermal analysis (SIA) has been carried out from simulated curves. It has been shown that in the case of ‘ n order’ and diffusion controlled reactions SIA curves approach to CRTA traces as the lower and upper reaction rate thresholds becomes closest. However, the shape of the SIA α - T plots of solid state reactions following an Avrami–Erofeev mechanism is quite different of

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the corresponding CRTA plot. A long isothermal steps is maintained at the temperature at which the higher threshold of the SIA experiment is reached and, therefore, the reaction rate is not maintained constant along the experiment.

It has been shown that SCTA methods, contrarily to rising temperature procedures, allow not only to discriminate between the different types of kinetic models from the analysis of the shape of a single α - T profile, but also to determine the activation energy and the pre-exponential factor of the Arrhenius equation from a single experiment excepts in the case of 'n order' reactions. In such a case the value of E/n instead of E is obtained from a single SCTA experiment and a previous knowledge of either the value of n or E for a complete kinetic analysis would be necessary. This uncertainty would be resolved by determining E under 'rate jump' conditions.

It is noteworthy to point out that the ability of SCTA methods for discriminating the kinetic model of solid state reactions with considerably higher precision than conventional isothermal or non-isothermal methods is not the only advantage of SCTA. The precise control of the reaction rate implies a control either direct or indirect of both the partial pressure of the gases generated or consumed in the reaction and the heat evolution rate, which allows to minimize the influence of heat and mass transfer phenomena and, therefore, to obtain kinetic parameters really closest to those of the forward solid state reaction. The ability of SCTA for controlling the surrounding atmosphere and minimizing the thermal gradients across the sample has been used for many authors for synthesising materials with controlled texture and structure. Thus, it has been reported in literature that it is possible to tailor the phase composition and the porosity of Al_2O_3 and Fe_2O_3 by controlling the decomposition rate and the partial pressure of the water vapour generated during the thermal decomposition of the corresponding hydroxides or oxy hydroxides used as precursors. It has been also shown that the use of SCTA method for the synthesis of barium titanate and silicon nitride from the thermal decomposition of barium titanyl citrate and the carbothermal reduction of silica, respectively, permits to control the phase composition and the crystal shape of the final products. Thus, the control of the barium titanyl citrate decomposition at a low enough rate leads to the synthesis large ribbons of BaTiO_3 constituted by welded nanocrystals, which improves the dielectric properties of the compacted bodies manufactured from these raw materials. Application of SCTA to the synthesis of oxides with high surface areas, sepiolites with controlled interfiber porosity and processes of thermal curing for improving the mechanical properties of cements, etc. have been described.

References

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