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Note

Investigation of the crystallization kinetics of cyclotetramethylenetetranitramine from nitric acid by microcalorimetry

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Abstract

The total heat produced and the rate of heat production during the crystallization of cyclotetramethylenetetranitramine (HMX) from nitric acid are measured using a conduction calorimeter. The data of thermograms of HMX are treated based on the dislocation theory model. The results show that the crystal growth process of HMX accords with the dislocation theory.

Keywords: Crystallization kinetics; Dislocation theory; HMX; Microcalorimetry

1. Introduction

In our previous paper [1], the crystallization kinetics of cyclotetramethylenetetranitramine (HMX) from *n*-C_7H_{16}/CCl_4(1:1, v/v) were studied. In order to obtain more information on the crystallization kinetics of HMX, we measured the total heat produced and the rate of heat production during the crystallization of HMX from HNO_3 at 34°C using a conduction calorimeter.

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Table 1
Total heat produced and crystal growth kinetics of HMX

Temp. (in °C)	Solute (in g)	Solvent (in g)	Seed (in g)	Diluent (in g)	Q_∞/(J g^{-1})	$dQ/dt = k_2(1 - Q/Q_\infty) + a$			$dm/dt = km_\infty(C - C_\infty) + b$	
						k_2	a	r	$k \times 10^2$	$b \times 10^6$
34	HMX (0.3648)	HNO_3 (2.8685)	–	H_2O (0.7910)	257	22.3	−0.21	0.99	2.39	−8.2
					270	24.6	−0.46	0.99	2.31	−15.7
				Mean	264	23.4	−0.34		2.35	−12.0
34	HMX (0.3819)	HNO_3 (2.8685)	HMX (0.2089)	H_2O (0.7910)	268	25.1	−1.34	0.95	2.35	−50.0
					253	47.5	−4.73	0.97	4.71	−187
				Mean	261	36.3	−3.04		3.53	−119

Q_∞, total heat produced (J g^{-1}); dQ/dt, rate of heat production at time t (J s^{-1}); k_2, rate constant of crystal growth (J s^{-1}); Q, heat production at time t (J); a, constant; dm/dt, rate of crystal growth at time t (g s^{-1}); k, rate constant of crystal growth (s^{-1}); m_∞, total mass of solid deposited (g); C, solute concentration in the solution (g/100 g solvent); C_∞, equilibrium saturation concentration (g/100 g solvent); b, constant.

2. Experimental

2.1. Materials

The HMX used as solute was prepared by our Institute and contained no detectable RDX. Its purity was more than 99.9%. The concentration of HNO_3 used as solvent was 95.68%. Twice-distilled water was used as diluent.

2.2. Equipment

All measurements are made using a conduction calorimeter, type RD-1 from Sichuan University, with a precision of $\pm$ 0.5% and equipped with two 60 ml vessels. The total heat produced, rate of heat production and rate of crystal growth were determined as described previously [1].

3. Results and discussion

Table 1 shows the total heat produced and crystal growth kinetics of HMX from HNO_3 at 34°C.

Because the values of the constants a and b are small in comparison with those of k_2 and k, the kinetics of the crystal growth process of HMX can be expressed by the equations

$$\frac{dQ}{dt} = k_2\left(1 - \frac{Q}{Q_\infty}\right)$$

$$\frac{dm}{dt} = k m_\infty (C - C_\infty)$$

This indicates that the crystal growth process of HMX from HNO_3 accords with the Burton–Cabrera–Frank dislocation theory [2].

References

[1] Chen Xijun, Li Zhibin and Hu Rongzu, Thermochim. Acta, 173 (1990) 193.
[2] W.K. Burton, N. Cabrera and F.C. Frank, Phil. Trans. R. Soc. London, Ser. A, 243 (1951) 299.