Journal of Thermal Analysis and Calorimetry, Vol. 80 (2005) 515–518

THERMAL HAZARD ANALYSIS OF HYDRAZINE AND NITRIC ACID MIXTURES

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In order to obtain a better understanding of the thermal hazard of hydrazine and nitric acid mixtures which are used in PUREX (Plutonium and Uranium Recovery by EXtraction) process during recycling of spent fuel in nuclear plant, DSC and small scale reaction calorimetry super-CRC were carried out for the mixtures in various conditions. From the DSC analysis the apparent activation energy of hydrazine monohydrate in SUS 303 crucible was determined to be 96 kJ mol^{-1}. The mixing hazard of hydrazine monohydrate with nitric acid was measured with super-CRC and the results suggested that the concentration and the mass of nitric acid had a strong influence on the mixing heat of reaction of the system.

Keywords: *DSC, hydrazine, mixing hazard, nitric acid, super-CRC*

Introduction

Chemical reaction hazards from exothermic reactions are one of the major hazards faced in the production of bulk and fine chemicals. In the absence of an understanding of these hazards, it is possible to develop conditions that lead to a thermal runaway reaction. In a study of past accidents, it was determined that inadequate understanding of the process chemistry and thermochemistry was a major contributing factor in almost 30% of the accidents [1]. Due to the severity of the risk involved in a thermal runaway reaction, a through understanding of the thermal risk of new processes is necessary [2, 3].

Also in the nuclear fuel reprocessing plant some events and accidents due to chemical reactions have been reported such as Savannah River or Tomsk-7 [4] and the demand of evaluation of chemical reactions has been increasing. The nuclear fuel reprocessing can be divided into two methods; the wet method and the dry method. PUREX (Plutonium and Uranium Recovery by EXtraction) method is the main current of wet reprocessing method in industrial scale. In this method the spent nuclear fuel is dissolved by nitric acid and extracted using tri-*n*-butyl phosphate ($C_{13}H_{27}PO_4$) as an organic solvent with *n*-dodecane ($C_{12}H_{26}$) as a diluent. In a Pu purification process after separation nitrate solution of uranium (U(IV)) or hydroxylamine (NH_2OH) are used as a reducing agent with hydrazine (N_2H_4) as an inhibitor of decomposition of uranium or hydroxylamine by nitrous acid. In a Pu concentration process after Pu purification process it is pointed out that Pu concentration might have a hazard of thermal instability and runaway due to the mixing reaction of hydrazine with excess nitric acid [5–7].

In this paper to obtain a better understanding of the thermal hazard of nitric acid and hydrazine mixtures which are used in PUREX process during recycling of spent fuel in nuclear plant, DSC and small scale reaction calorimetry were carried out for the mixtures in various conditions. At first DSC was carried out for the hydrazine monohydrate with SUS 303 stainless steel closed crucible and gold plated crucible and the influence of the vessel material and also the heating rate were studied. Next the mixing hazard of hydrazine monohydrate and nitric acid with different concentrations was investigated with the small scale reaction calorimeter super-CRC of Omnical Co. Ltd. at the constant temperature.

Experimental

Materials

Materials used in this study were hydrazine monohydrate ($N_2H_4{\cdot}H_2O$; HH) and nitric acid (HNO_3; NA). Both were reagents from Wako Chemicals Co. Ltd., and were used without further purification and prepared as desired concentration with deionized water.

As a preliminary study thermochemical calculation of HH and fuming NA mixture was done with REITP-3 program and the maximum heat of reaction and its composition were estimated as 272 kJ mol^{-1} of

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1388–6150/$20.00

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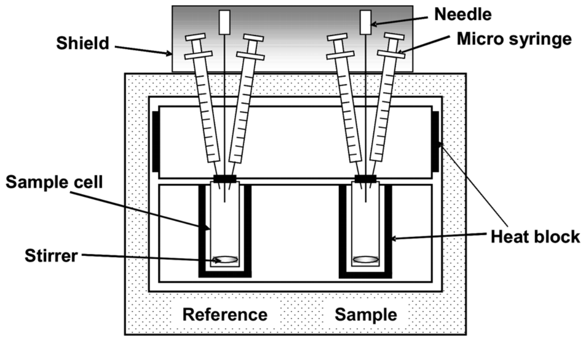

Fig. 1 Schematic diagram of reaction calorimeter super-CRC

reactants (= 5,900 J g^{-1} of reactants) and 38 mass% of HH, respectively [8, 9].

Thermal hazard of HH with DSC

Thermal hazard of HH during heating was determined with pressure DSC 827e of Mettle Toledo. 1.5 to 2.5 mg of the sample was heated up from room temperature to 573 K and a heating rate was varied from 1 to 20 K min^{-1}. The closed crucible made by the austenitic stainless steel (SUS 303) specified in JIS G 4303–4307 and the gold plated closed crucible were used to investigate the influence of the vessel material under 0.1 MPa air atmosphere. Chemical composition of SUS 303 is shown in Table 1.

Mixing hazard of HH and NA with super-CRC

The isothermal mixing hazard of HH with nitric acid was investigated using a small scale reaction calorimeter super-CRC of Omnical Co. Ltd. [10]. Figure 1 shows a schematic diagram of super-CRC. In this series of test 1 g of HH was injected into the 16 mL glass vessel where pre-heated excess amount of NA was stirred. The mass and the concentration of NA were varied as 9, 5, 1 g and 1.0, 3.0, 5.0 mol L^{-1} respectively and the temperature of the vessel was kept at 320 K.

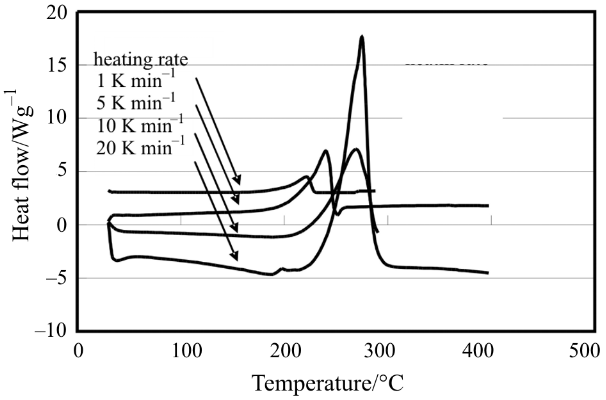

Fig. 2 Influence of heating rate on DSC curves of hydrazine hydrate with SUS 303 closed crucible

Data analysis was performed using the software provided by Mettler Toledo and Ominical for respective instruments.

Results and discussion

Thermal hazard of HH with DSC

Figure 2 shows the DSC curves of HH in SUS 303 closed crucible with different heating rate and Table 2 shows the summary of DSC measurement. The onset temperature and the heat of reaction in the table is the average value of at least 2 runs for each condition. Concerning the data with SUS 303 closed crucible the onset temperature increased with the increase of the heating rate, whereas the heat of reaction was almost in the same level as about 1800 J g^{-1}. Since SUS 303 is less active with HH than usual metal except chro-

Table 1 Chemical composition of SUS 303 stainless steel

Element	C	Si	Mn	P	S	Ni	Cr
content/mass%	<0.15	<1.00	<2.00	<0.20	<0.15	8.00~10.00	17.00~19.00

Table 2 Influence of crucible material and heating rate on the DSC results of HH

Heating rate/K min^{-1}	SUS 303 closed crucible		gold plated closed crucible	
	onset temperature/K	heat of reaction/J g^{-1}	onset temperature/K	heat of reaction/J g^{-1}
1	464	2020	436	*
5	488	1810	444	*
10	504	1830	451	(1220)**
20	528	1790	458	*

*not detreminable; **unconfirmed

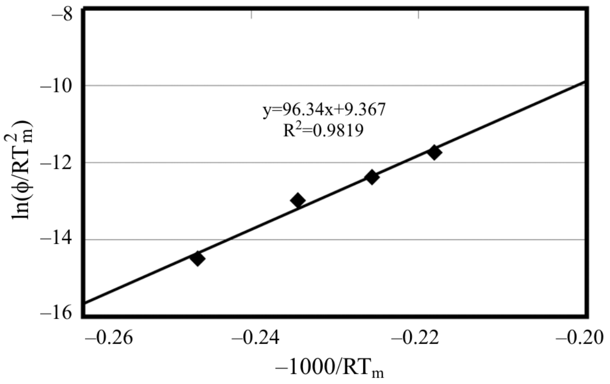

Fig. 3 Kissinger plot of hydrazine hydrate with SUS 303 closed crucible

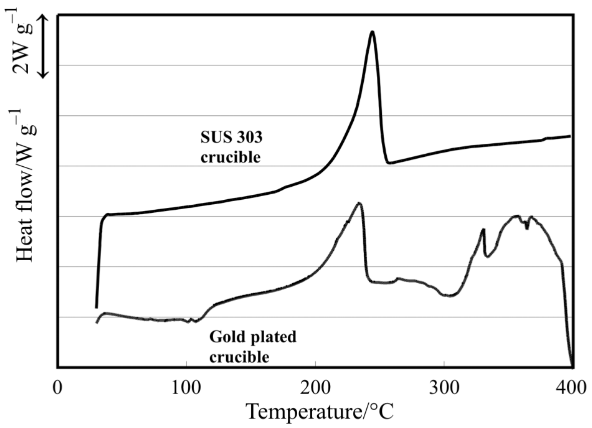

Fig. 4 DSC results of hydrazine hydrate with SUS 303 crucible and with gold plated crucible

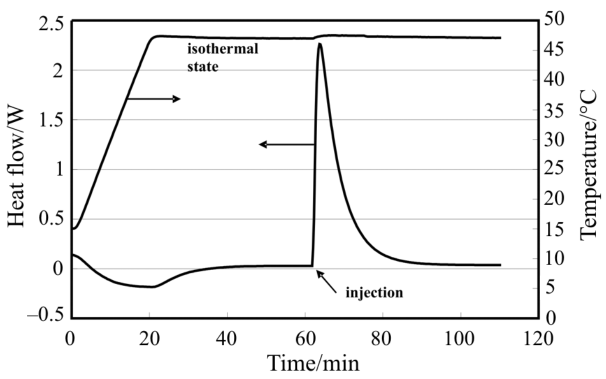

Fig. 5 Typical heat flow profile of 1 g hydrazine hydrate mixed with 9 g of 5 M nitric acid

mium, aluminum or SUS 316L because of the passivization of the surface due to the existence of chromium [5]. Figure 3 shows the Kissinger plot of HH with SUS 303 crucible and the apparent activation energy was determined to be 96 kJ mol^{-1} which showed a good agreement with the reported data of many scientists, which were around 100 kJ mol^{-1} [5].

Regarding the influence of the crucible material DSC was carried out for the HH with SUS 303 and gold plated crucible. A typical DSC curve with gold plated crucible with a heating rate of 10 K min^{-1} is shown in Fig. 4 with the DSC curve with SUS 303 crucible in the same condition. The DSC results are summarized in Table 2. DSC curve with gold plated crucible showed less repeatability and the onset temperature was lower than that with SUS 303 crucibles. It was considered that HH reacted with the gold plated crucible. Kowhakul *et al.* reported the onset temperature of DSC at a heating rate of 10 K min^{-1} of hydrazine solution of 2 mol L^{-1} with the gold plated crucible as 485 K and that with glass capillary cell as 620 K, and the activation energy determined with Ozawa method as 38.2 kJ mol^{-1} and 140.5 kJ mol^{-1} respectively [11]. They used a diluted hydrazine solution and the onset temperature with gold plated crucible showed rather higher value than our work at the same heating rate as them, which was 451 K shown in Table 2. According to the relative activity of metal powders on the catalytic decomposition of liquid hydrazine gold has 18 times larger influence as SUS 304L, 78 times larger than chromium and 130 times larger than tantalum [12].

Although Askey first reported the thermal decomposition scheme of HH vapor with silica and platinum and tungsten as follows [13], investigation in liquid phase is very few.

HH in silica vessel:

$$3N_2H_4 \rightarrow N_2+4NH_3 \text{ (at 571 K)} \tag{1}$$

HH on platinum and tungsten:

$$2N_2H_4 \rightarrow N_2+H_2+2NH_3 \text{ (at 478 K)} \tag{2}$$

It is concluded that gold have a stronger influence on the decomposition behaviour of HH than SUS 303 and experiments in glass vessel is more suitable to study the thermal behaviour.

Mixing hazard of HH and NA with super-CRC

Figure 5 shows a typical heat flow profile of HH when mixed with NA measured with a super-CRC. The upper line indicates the temperature of the contents of the equipment and the lower line indicates the heat flow. Nitric acid was linearly heated up to 320 K within 20 min after the beginning of the heating and was kept at isothermal condition as the same value through the experiment. The heat flow first shows the concave peak until 30 min from the beginning of heating which corresponds to a heating stage and that shows an apparent endotherm. After the heat flow recovered to a baseline and the temperature equilibrium was established, which took about 60 min from the beginning, 1 g of HH was injected into 9 g of

Table 3 Heat of reaction of HH/NA system determined by super-CRC

HH/NA	NA 1 mol L^{-1}	 3 mol L^{-1}	 5 mol L^{-1}
1/1 g	146	200	266
1/5 g	283	560	916
1/9 g	398	779	1235

unit: J g^{-1} – hydrazine hydrate

5 mol L^{-1} NA in a glass vessel. The heat flow showed a sharp exothermic peak immediately after the addition and reached about 2.3 W/g^{-1} of HH followed by a relaxation process and the positive heat flow lasted for about 25 min. The heat of reaction was determined as 1.235 J/g^{-1} of HH. The heat flow profiles were found as similar pattern as in all other mixtures and it was considered that the reaction proceeded in the same manner. Table 3 shows mixing heats of reaction of HH and NA in various conditions and the heat of reaction increased with the increase of the concentration of the nitric ion which reacted with HH in the mixtures [14, 15]. As the mixing hazard consists of the instantaneous hazard and the hazard which is seen afterwards chemical analysis of the reaction products and the reaction scheme are needed for detail discussion. It is found that the concentration and the mass of NA have a strong influence on the heat of reaction of HH and NA system and super-CRC is a useful tool to investigate the mixing hazard of the solution.

Conclusions

From the experimental investigation of DSC and small scale reaction calorimeter super-CRC on hydrazine monohydrate and nitric acid mixtures following conclusions can be drawn:

- Vessel material has a strong influence on the decomposition of hydrazine monohydrate.
- From the DSC data analysis the apparent activation energy of thermal decomposition of hydrazine monohydrate was determined to be 96 kJ mol^{-1} and it showed a good agreement with the published data.
- From the calorimetric data the concentration and the mass of NA have a strong influence on the heat of reaction of HH and NA system and super-CRC is a useful tool to investigate the mixing hazard of the solution.

Acknowledgements

This work was supported by a Grant-in-Aid for the Advanced Fundamental Research from the Japan Nuclear Cycle Development Institute.

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