Journal of Nuclear Materials 393 (2009) 497–503

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Decomposition and multiphase reactions in the system $UO_2(NO_3)_2 \cdot 6H_2O–Ni(NO_3)_2 \cdot 6H_2O$ at elevated temperatures

Bhupesh B. Kalekar *, K.V. Rajagopalan, P.V. Ravindran

Analytical Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

ARTICLE INFO

Article history:
Received 25 February 2009
Accepted 22 July 2009

ABSTRACT

Solid state reactions between uranyl nitrate hexahydrate and nickel nitrate hexahydrate in mixtures of various ratios have been studied at elevated temperatures. The binary system of uranyl nitrate hexahydrate and nickel nitrate hexahydrate was found to form a eutectic of composition 53 mol% uranyl nitrate hexahydrate and 47 mol% nickel nitrate hexahydrate at 40 °C. The overlap of evolution of nitric oxide (NO) and water vapour above 230 °C confirmed the presence of hydroxynitrates of uranium and nickel as intermediate products. These hydroxynitrates began to react above 280 °C to form nickel uranate, NiU_3O_{10}, in the case of mixtures containing 75 mol% uranyl nitrate hexahydrate. When the proportion of uranyl nitrate hexahydrate in the mixture was higher than 75 mol%, U_3O_8 formed along with nickel uranate. For the mixtures containing uranyl nitrate hexahydrate lower than 75 mol%, NiO was observed to form along with NiU_3O_{10}.

1. Introduction

The nitrates of uranium and nickel are present in high level nuclear waste along with those of other fission, corrosion and actinide products [1]. The studies of multiphase interactions of these nitrates at high temperatures are important for characterizing kinds of intermediate nitrato-complexes related to their thermal stabilities which are required to optimize the calcination conditions for the conversion of nitrates to oxides. The conversion calcination is an important process before the immobilization of the waste in glass form. In order to improve this process, one need to have a reliable database for the conversion reactions of various nitrate mixtures relevant to high level nuclear wastes at elevated temperatures.

In the course of our studies on the phase equilibria of the systems, uranyl nitrate hexahydrate (UNH) – sodium nitrate and UNH – strontium nitrate, it has been shown that a number of reactions take place between the compounds and/or their decomposition products on heating, including the formation of various intermediate nitrato-complexes of different thermal stabilities [2,3]. The mixed oxides formed by the decomposition of these nitrato-complexes vary in stoichiometry depending on the initial composition of the mixtures in the UNH–strontium nitrate system. The complex nature of interactions in these pseudobinary systems necessitates detailed studies on the other binary, ternary and multicomponent nitrate mixtures for better understanding of the reactions which occur during the denitration of high level liquid waste.

Nickel nitrate is used as the precursor material for the preparation of nickel oxide. Nickel oxide is widely used for the preparation of catalysts and molecular sieves [4,5]. Various research workers have reported the thermal decomposition mechanisms of nickel nitrate hexahydrate at elevated temperatures [6–11]. Similarly, UNH, its intermediate products and subsequent stable oxides at higher temperatures have also been studied [12,13]. However, the data on binary nitrate mixtures of UNH and nickel nitrate hexahydrate (NNH) at elevated temperatures have not yet been reported. In this paper, the reactions between UNH and NNH at elevated temperatures have been studied using simultaneous TG–DTA–EGA (Thermogravimetry–Differential Thermal Analysis–Evolved Gas Analysis) and XRD (X-ray diffraction) techniques. The reactions have been discussed using the results of these measurements.

2. Experimental

UNH was prepared from nuclear grade U_3O_8 [12] and analytical reagent grade NNH was obtained from Himedia Laboratories, India. These compounds were checked by TG and XRD measurements. Mixtures of UNH with NNH containing 20, 30, 40, 50, 60, 70, 75 and 80 mol% UNH were prepared by mixing the weighed amounts of component nitrates and grinding gently in a mortar and pestle. The TG–DTA–EGA measurements were carried out on 100 mg samples in dynamic argon atmosphere (80 mL/min) using Netzsch thermal analyzer (Model STA-409) coupled to Balzers quadrupole mass spectrometer (Model QMG-311) via a heated capillary [12]. Specimen holders used were those made of recrystallised alumina. Heating rate was 10 K/min for all measurements.

---

* Corresponding author. Tel.: +91 2225593291; fax: +91 2225505151.
E-mail address: bhupkal@barc.gov.in (B.B. Kalekar).

0022-3115/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2009.07.011

The intermediate compounds for XRD measurements were prepared in situ in the thermal analyzer by heating the mixtures under conditions identical to normal TG–DTA experiments and switching off the furnace power after attaining the desired temperatures. The argon flow was maintained until the samples cooled to room temperature. All XRD measurements were carried out on a Philips X-ray diffractometer (Model PW1710) using nickel-filtered Cu-Kα radiation.

3. Results and discussion

Both UNH and NNH melt at 65 °C [12,9]. The first peak on DTA curves in Fig. 1 for UNH, NNH and their mixtures represents melting. The extrapolated on-set temperature of DTA peaks was used as measure of the melting temperature. Duplicate measurements were carried out and the averaged values of extrapolated on-set temperatures were obtained. The temperature values for the mixtures were lower than those for UNH and NNH. The variation of the extrapolated on-set temperature for different mixtures containing 0, 20, 30, 40, 50, 60, 70, 80 and 100 mol% UNH confirmed the formation of a eutectic of 53 mol% UNH–47 mol% NNH at 40 °C (Fig. 2).

The DTA peaks observed in the temperature range of 40–230 °C are different in number for UNH, NNH and UNH–NNH mixtures (Fig. 1). Apart from the melting peak, two peaks with peak temperatures of 140 and 190 °C and a shoulder peak at 210 °C are observed in the case of UNH. The peak at 140 °C is the most intense among these. NNH, on the other hand, shows a large endothermic

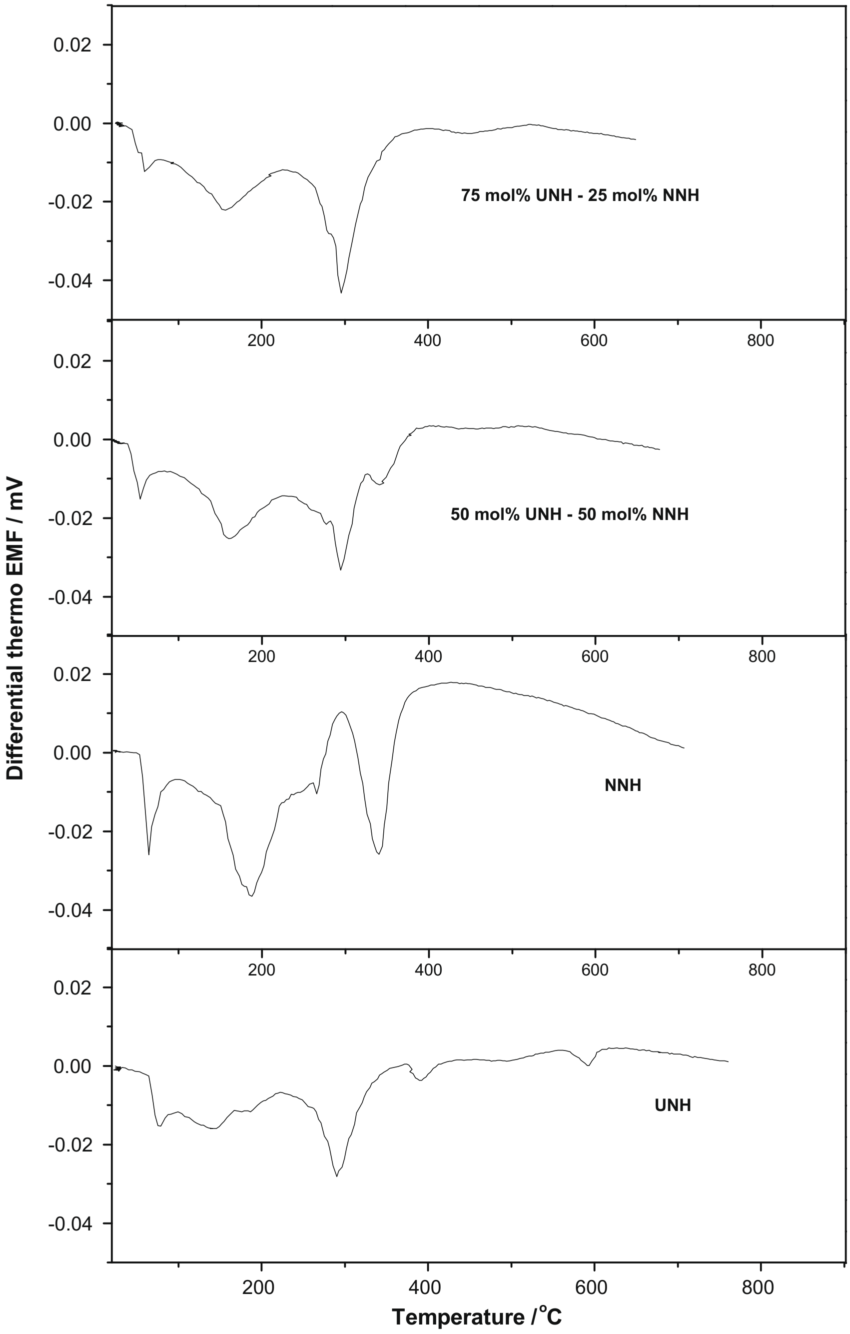

Fig. 1. DTA curves for UNH, NNH, 75 mol% UNH–25 mol% NNH mixture and 50 mol% UNH–50 mol% NNH mixture recorded at a heating rate of 10 K/min.

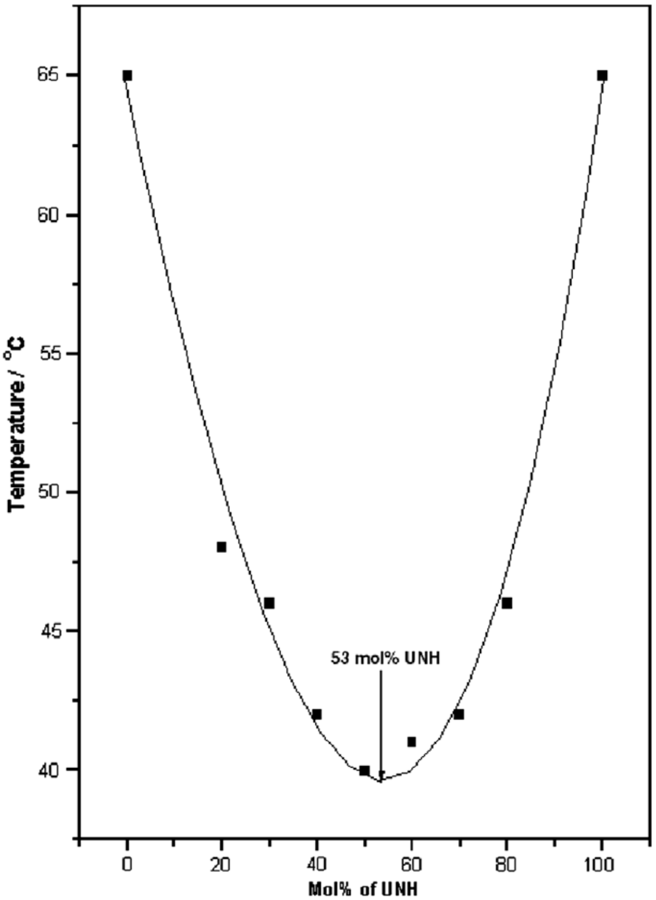

Fig. 2. Extrapolated on-set temperature of melting peaks of UNH, NNH and their mixtures in various mol ratios plotted against mol% of UNH.

peak with a peak temperature of 190 °C and a small shoulder peak at 150 °C in addition to the melting peak in this temperature range. For UNH–NNH mixtures, only one clear dehydration event with a peak temperature of 160 °C is seen. The dehydration events with peak temperatures of 150 and 190 °C in NNH correspond in temperature with the dehydration events in UNH at 140 and 190 °C, respectively. But, for a given sample weight the dehydration peak of NNH at 190 °C is more intense than those of UNH and UNH–NNH mixtures. The small peaks at 190 and 210 °C observed for UNH could be missed for UNH–NNH mixtures because of decreased UNH content of the samples.

The EGA data for water vapour and nitric oxide evolved from the samples over the reaction intervals recorded simultaneously with the TG–DTA measurements using a mass spectrometer coupled with the thermal analyzer are presented in Fig. 3. The ion current in the mass spectrometer due to H_2O^+ ion (mass to charge ratio, $m/e = 18$) shows a continuous drift with a negative slope due to the effect of vacuum on the background moisture level and this drifting signal defines the trend line for baseline signal in the reaction interval. The drift occurs due to "virtual leak" arising from continuous desorption of water vapour, pre-adsorbed during the switched off condition of the instrument, into the ionization chamber of the mass spectrometer. This is more prominent in the case of gases, like, water vapour which condense at normal temperature and pressure than for permanent gases. The large baseline drift may cause difficulties in identifying the gas evolution peaks, especially when the background level is high and the peaks are small. Subtraction of background using the measured blank data, however, was not made here because of poor reproducibility of the background levels in the present measurements. An alternative is to draw the trend line using the slope of the drifting baseline and identify regions where the signal shows positive deviation from the trend line. During gas evolution from the sample, the signal will deviate above the trend line, reach a maximum level and then slowly decay back to the trend line after the reaction. In the decomposition curve of 75 mol% UNH–25 mol% NNH mixture shown in Fig. 3, two overlapping water evolution peaks are observed in the temperature ranges of 80–230 and 230–380 °C with peak temperatures of 160 and 290 °C, respectively. The first of these corresponds to the dehydration step and the latter is due to dehydroxylation of hydroxynitrates. The peak temperature of the first EGA peak for water vapour is close to the peak temperature of the second DTA peak for 75 mol% UNH–25 mol% NNH mixture.

The TG curve for 75 mol% UNH–25 mol% NNH mixture showed a perceptible break/change in the slope over the temperature interval 200–250 °C indicating overlap of two reactions. A weight loss of 16.1% was observed in the temperature range 60–230 °C corresponding to the release of 16 water molecules out of 24 molecules available in the 3:1 (UNH: NNH) mixture (Fig. 4a).

The denitration reactions of UNH as well as 75 mol% UNH–25 mol% NNH mixture initiated at the same temperature of 230 °C (Figs. 1 and 3). However, the EGA curve of NNH for nitric oxide (NO) showed the evolution starting at 205 °C. These results indicate a small enhancement in thermal stability of NNH in the presence of UNH. The evolution of nitric oxide from UNH–NNH mixtures occurred in multiple steps in the temperature range 230–550 °C. The first NO evolution peak, in the range 230–400 °C, was sharp and corresponding to the major denitration step. It was also accompanied by evolution of water vapour (Fig. 3). The overlap of the evolution of NO and H_2O above 230 °C confirmed the presence of hydroxynitrates of uranium and nickel. The hydroxynitrates are those formed by the hydrolysis of the nitrates in presence of water vapour accumulated around the hydrate particles in the bulk of the sample during the dehydration step. The flow of argon around the sample holder employed in TG–DTA–EGA experiments was not efficient enough to drive the water vapour from the bulk of the dehydrating sample. The nature and stoichiometry of the hydroxynitrates will depend on the extent of hydrolysis and thus on the amount and standing time of water vapour over the sample particles. These hydroxynitrates decomposed to give multiple evolution peaks of nitric oxide in EGA depending on their stability and stoichiometry. The EGA curves for UNH are identical to those reported earlier and attributed to the decomposition of hydroxynitrates formed by hydrolysis and polymerization due to the effect of water vapour accumulated around sample particles during dehydration [12].

The intermediate hydroxynitrate, $Ni(OH)NO_3 \cdot ½H_2O$, has been reported to be formed at 280 °C during the decomposition of NNH [8]. The TG curve of NNH indicated a change in slope tending towards plateau region around 280 °C (Fig. 4b). The DTA curve for NNH presented in Fig. 1 showed a shoulder peak at 265 °C. The EGA curve for NO evolution from NNH presented in Fig. 3 showed a clear peak at 280 °C. The DTA curve of 75 mol% UNH–25 mol% NNH mixture also showed a small shoulder at 280 °C (Fig. 1). This shoulder peak was better resolved in 50 mol% UNH–50 mol% NNH mixture. After the initiation of weight change due to denitration at 230 °C, the TG curve for the 75 mol% UNH–25 mol% NNH mixture also showed a change in slope tending towards a small plateau region around 280 °C (Fig. 4a). The TG curve of UNH corresponding to the first NO evolution step in Fig. 4c shows a weight loss step in the temperature range of 225–325 °C with maximum slope (rather than plateau) around 290 °C (matching with peak points in DTA and EGA curves). Subsequently, the slope decreases and tends towards a plateau by around 325 °C. The plateau at around 280 °C

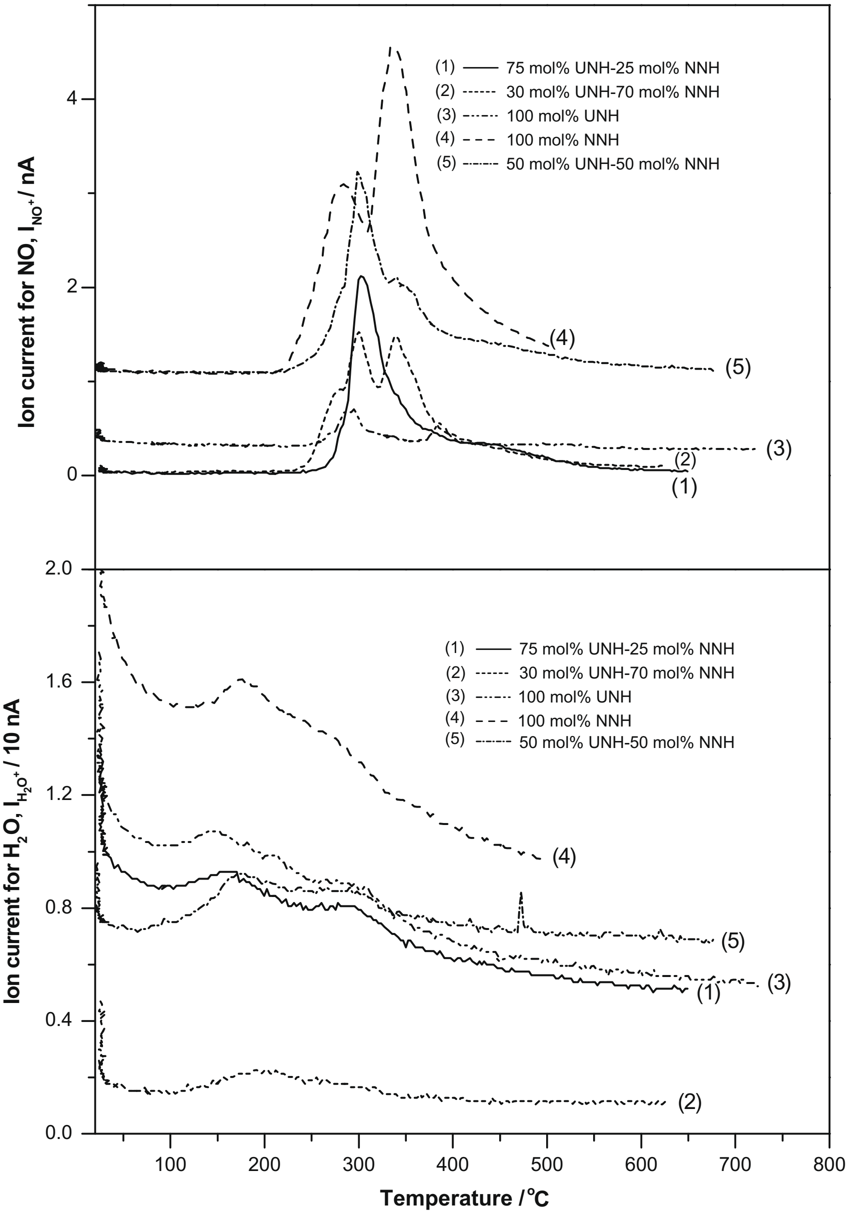

Fig. 3. EGA evolution profile of H_2O and nitric oxide (NO) for UNH, NNH and their mixtures in various mol ratios.

is observed at about 45 °C lower temperature than the plateau corresponding to the end of first denitration step in UNH. Hence, the formation of the basic nitrate, $Ni(OH)NO_3 \cdot ½H_2O$ at around 280 °C can be inferred from our DTA, EGA and TG data for the mixtures. This result also suggests that the nitrates of uranium and nickel do not react up to the temperature of 280 °C.

The EGA curves for NO evolution, presented in Fig. 3, show two clear denitration events in each of NNH and UNH. The first peak of NNH, at 280 °C is due to the formation of nickel hydroxynitrate. The second peak, with a peak temperature of 340 °C, could be due to the decomposition of this hydroxynitrate to form NiO. The NO evolution pattern of UNH matches the results reported earlier [12] and shows EGA peaks with peak temperatures of 290 and 385 °C. Additionally, a shallow drawn out peak of very low intensity is also observed for UNH in the temperature range of 400–535 °C. For 75 mol% UNH–25 mol% NNH mixture, however, we observed only one clear NO evolution peak in the temperature range 230–400 °C with a peak temperature of 305 °C. The second denitration peak of NNH was absent in the EGA curve for 75 mol% UNH–25 mol% NNH mixture. This could be because the hydroxynitrates of uranium and nickel directly reacted in 3:1 mol ratio to give nickel uranate in the temperature range 280–400 °C. Thus, in case of the EGA curve for 75 mol% UNH–25 mol% NNH mixture, there was very little or no free nickel nitrate or uranyl nitrate left over above 400 °C. The shallow peaks in DTA and EGA for NO in Figs. 1 and 3 accompanied by a gradual weight loss up to about 550 °C may be due to small amounts of uranyl hydroxynitrate [12] left unreacted due to heterogeneous nature of the process. When the proportion of NNH in the mixture was such that UNH/NNH < 3, the second denitration event in excess amount of NNH was observed at 340 °C. This is evident from EGA curves for 30 mol% UNH–70 mol% NNH and 50 mol% UNH–50 mol% NNH mixtures in Fig. 3. The DTA curve for 50 mol% UNH–50 mol% NNH mixture presented in Fig. 1 also shows an endothermic peak with a peak temperature of 340 °C corresponding to the second denitration event in NNH, but the same is missing in the DTA curve

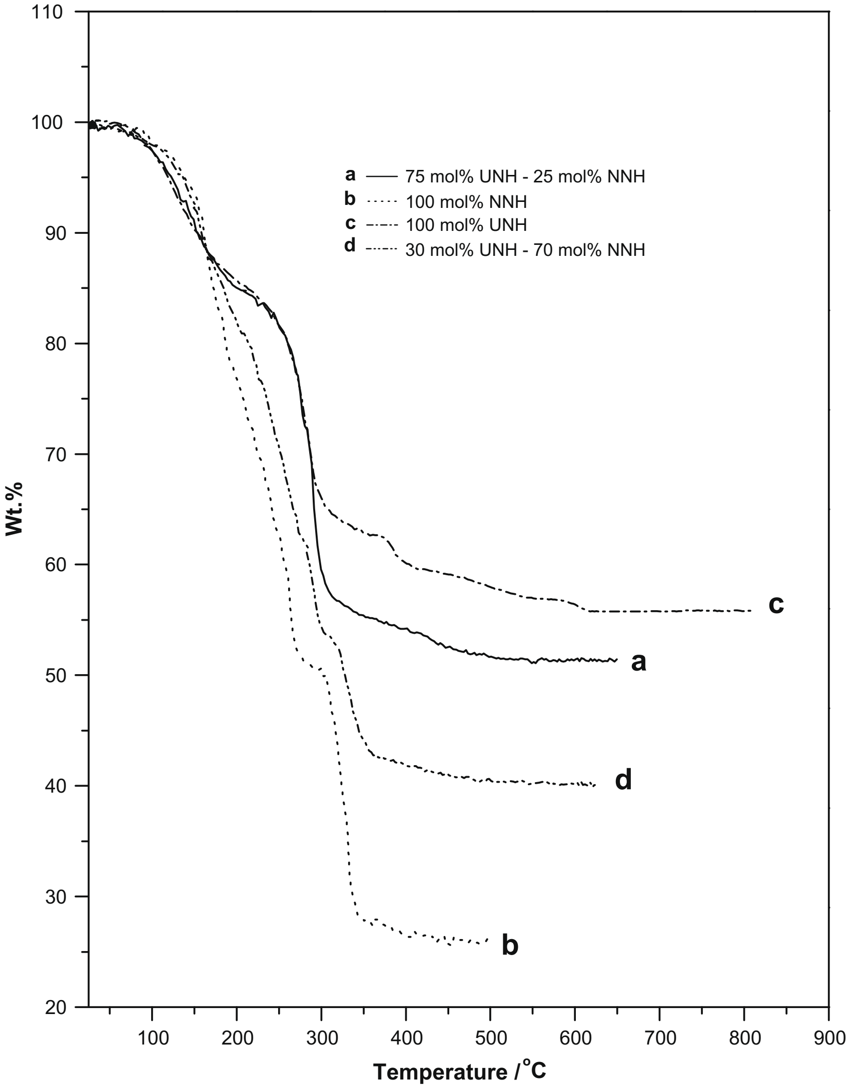

Fig. 4. TG curve for 75 mol% UNH–25 mol% NNH and 30 mol% UNH–70 mol% NNH mixtures heated at a heating rate of 10 K/min.

for 75 mol% UNH–25 mol% NNH mixture. In the case of UNH/NNH > 3, the amount of unreacted hydroxynitrate of uranium left over above 400 °C was small and since the intensities of denitration events in UNH above 400 °C were very small, these reactions could not be clearly observed.

The DTA curve for UNH in Fig. 1 shows a small endothermic event in the temperature range 565–615 °C with a peak temperature of 590 °C. This has been attributed to the self reduction of UO_3 to U_3O_8 [12]. The absence of this peak in case of UNH–NNH mixtures should be attributed to the conversion of most of uranyl nitrate to nickel uranate before 565 °C. Any UO_3 remaining unreacted at this temperature is too little to be detected as the self reduction peak in DTA. The data presented here thus indicate that the reaction between UNH and NNH to form nickel uranate takes place in 3:1 mol ratio. Total weight loss of 48.8% observed up to 550 °C from TG curve for 75 mol% UNH–25 mol% NNH mixture also supported the conclusion on formation of the nickel uranate before the initiation of self reduction of UO_3 at 565 °C.

Different samples of the mixture having the composition, 75 mol% UNH–25 mol% NNH were heated to 315, 400 and 550 °C and cooled to room temperature in argon atmosphere in order to characterise the residues by X-ray diffraction patterns. The result is presented in Fig. 5. The XRD pattern of the sample heated to 315 °C showed the formation of amorphous products, either partly decomposed hydroxynitrates or UO_3 [14]. The residue of 75 mol% UNH–25 mol% NNH mixture after heated to 400 °C, corresponding to the final temperature of the major denitration peak in Fig. 3, gave the XRD peaks showing the first appearance of the stable oxide phase, NiU_3O_{10} [15]. The major diffraction lines of NiU_3O_{10} could be observed clearly in the XRD pattern of the sample heated to 550 °C. The XRD data thus complement the results of thermoanalytical measurements.

The TG curve for 30 mol% UNH–70 mol% NNH mixture presented in Fig. 4d was horizontal up to 60 °C and showed small kinks at around 210 and 280 °C in the continuous weight loss pattern. A weight loss of 19.7%, due to dehydration, observed in the temperature interval 60–210 °C was in agreement, within normal experimental errors, with the theoretical weight loss of 20.33% for the release of two-third of the total 60 molecules of water of crystallization available in 3:7 mixture of UNH and NNH. This observation matched well with the weight loss observed on heating up to 230 °C in case of 75 mol% UNH–25 mol% NNH mixture. The formation of basic nitrate, $Ni(OH)NO_3{\cdot}\frac{1}{2}H_2O$, around 280 °C is indicated as small kink on the TG curve of 30 mol% UNH–70 mol% NNH mixture. The decomposition of nickel hydroxyni-

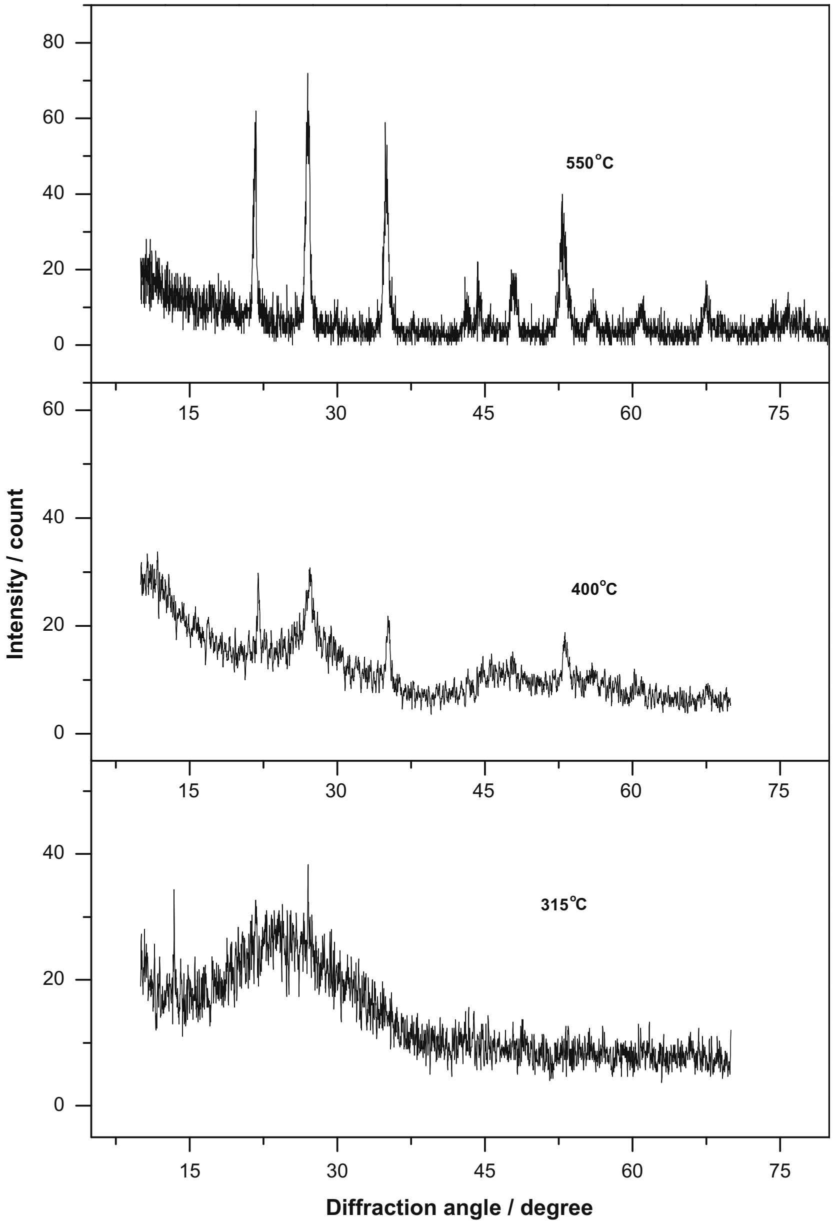

Fig. 5. XRD patterns for 75 mol% UNH–25 mol% NNH after heated at 315, 400 and 550 °C in argon.

trate, in excess of that required for the formation of NiU_3O_{10}, to form NiO is observed on the TG curve as a weight loss step in the range 310–370 °C. The total weight loss of 59.5% observed for this mixture in the temperature range of 60–450 °C is in fair agreement with the theoretical weight loss of 61% for the formation of a mixture of NiU_3O_{10} and NiO in the proportion 1:6 from the UNH–NNH mixture.

Fig. 6 shows the XRD patterns for 30 mol% UNH–70 mol% NNH and 80 mol% UNH–20 mol% NNH samples cooled to room temperature after heating in argon atmosphere. The pattern for 30 mol% UNH–70 mol% NNH mixture heated to 315 °C shows the peaks indicating the appearance of NiO [16]. On the other hand, the pattern for this mixture heated to 450 °C shows the formation of NiU_3O_{10} together with NiO. The formation of NiO is explained as caused from shortage of the amount of UNH to react with NNH to form NiU_3O_{10}. The stoichiometric reaction for NiU_3O_{10} formation takes place at UNH/NNH = 3 (75 mol% UNH–25 mol% NNH). The lowering of final temperature of formation of uranate phase could be due to insignificant amount of undecomposed nitrates left in 30 mol% UNH mixture at temperatures higher than 315 °C. The XRD pattern of the residue of 80 mol% UNH–20 mol% NNH mixture heated at 600 °C indicated the presence of U_3O_8 [17] along with NiU_3O_{10}. Since UNH/NNH > 3 in this case, the excess UNH is considered to have formed the binary oxide U_3O_8.

4. Conclusion

The binary mixture, $UO_2(NO_3)_2{\cdot}6H_2O$–$Ni(NO_3)_2{\cdot}6H_2O$ showed the formation of eutectic at the composition of 53 mol% of UNH–47 mol% NNH at a temperature of 40 °C. The hydroxynitrates of uranium and nickel formed during the denitration step react in 3:1 mol ratio to form nickel uranate, NiU_3O_{10}. Mixtures with composition other than 75 mol% UNH/25 mol% NNH gave U_3O_8 or NiO along with NiU_3O_{10} depending on whether the amount of UNH is larger or smaller than 75 mol%.

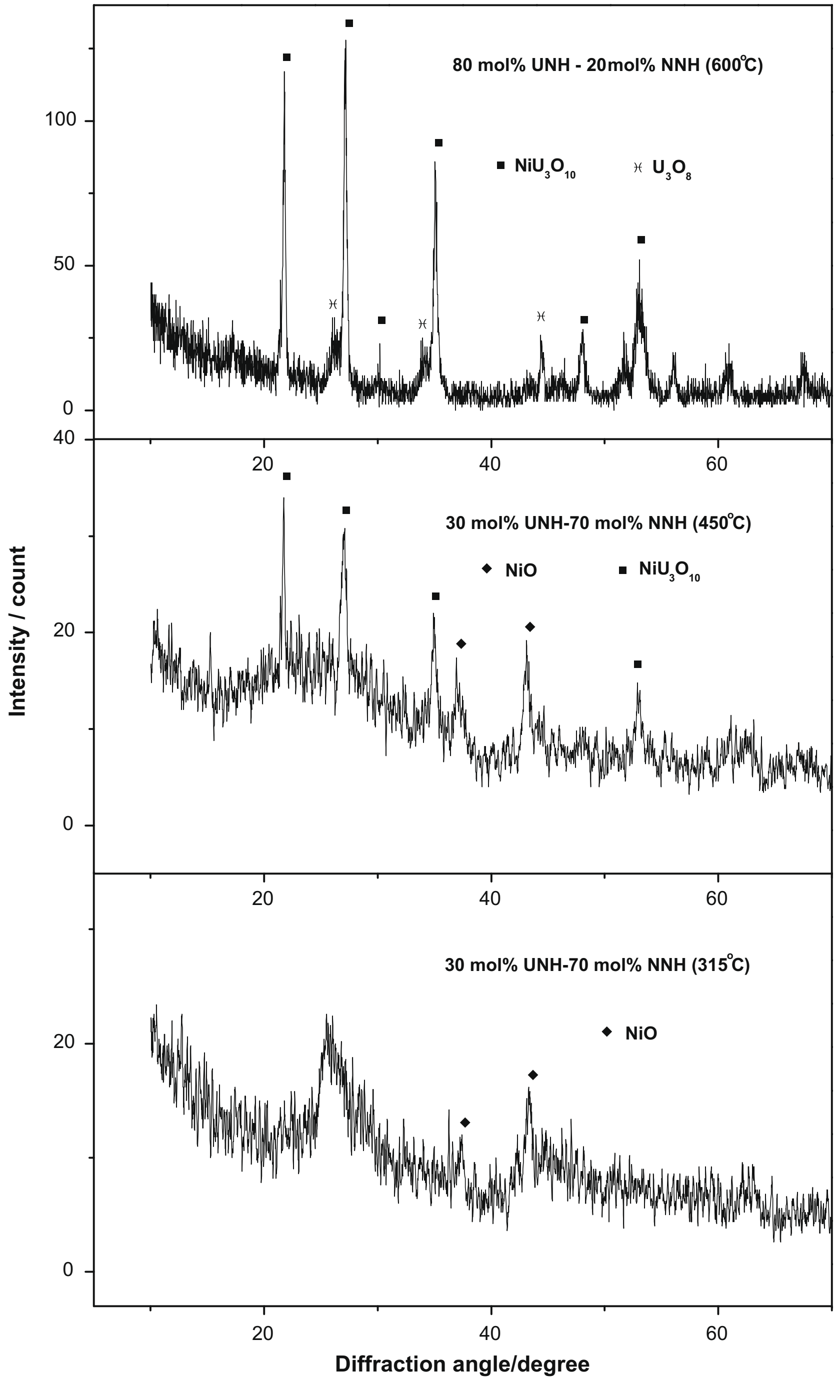

Fig. 6. XRD patterns for 80 mol% UNH–20 mol% NNH and 30 mol% UNH–70 mol% NNH mixtures after heated at 315, 450 and 600 °C in argon.

Acknowledgements

The authors thankfully acknowledge the help from Dr. D. Das, Head, Chemistry Division and Dr. A.K. Tyagi, Chemistry Division, BARC in recording the XRD patterns of the compounds.

References

[1] International Atomic Energy Agency Techniques for the solidification of HLW, Technical Report Series 176, IAEA, Vienna, 1979, p. 10.
[2] B.B. Kalekar, K.V. Rajagopalan, C.G.S. Pillai, P.V. Ravindran, P.K. Mathur, J. Nucl. Mater. 279 (2000) 245.
[3] P.V. Ravindran, B.B. Kalekar, K.V. Rajagopalan, C.G.S. Pillai, P.K. Mathur, J. Nucl. Mater. 317 (2003) 109.
[4] W.W. Wendlandt, Thermochim. Acta 10 (1974) 101.
[5] J. Mu, D.D. Perlmutter, Thermochim. Acta 56 (1982) 253.
[6] D. Dollimore, G.A. Gamlen, T.J. Taylor, Thermochim. Acta 91 (1985) 287.
[7] F. Paulik, J. Paulik, M. Arnold, Thermochim. Acta 121 (1987) 137.
[8] K. S. Chun, Atomic Energy Establishment Report, Report No. AERE-R-8735.
[9] S.A.A. Mansour, Thermochim. Acta 228 (1993) 173.
[10] A. Malecki, R. Gajerski, S. Labus, B.P. Kilsh, K.T. Wojcieschowski, J. Therm. Anal. 69 (2000) 17.
[11] W. Brockner, C. Ehrhardt, M. Gjikaj, Thermochim. Acta 456 (2007) 64.
[12] K.V. Rajagopalan, P.V. Ravindran, T.P. Radhakrishnan, J. Therm. Anal. 44 (1995) 89.
[13] C.C. Addison, H.A.J. Champ, N. Hodge, A.N. Norbury, J. Chem. Soc. (1964) 2354.
[14] R.S. Ondrejin, T.P. Garret Jr., J. Phys. Chem. 65 (1961) 470.
[15] JCPDS International Centre for Diffraction Data, Card No. 44-0978.
[16] JCPDS International Centre for Diffraction Data, Card No. 44-1159.
[17] JCPDS International Centre for Diffraction Data, Card No. 31-1425.