

# THERMAL DECOMPOSITION STUDIES OF PRE-IRRADIATED NICKEL (II) AZIDES.

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## ABSTRACT

The effect of pre-irradiation on the thermal decomposition of three samples of nickel (II) azide was studied. It was found that the rates of thermal decomposition of  $\text{Ni}(\text{OH})\text{N}_3$  increased substantially with increase in pre-irradiation dosage. The initial reaction rates change from time-dependent nucleation law for the unirradiated sample to a unimolecular decay law for the sample irradiated with heavy dosage. The activation energy of pre-irradiated  $\text{Ni}(\text{OH})\text{N}_3$  increased to  $117\text{KJ mole}^{-1}$  from  $106.2\text{KJ mole}^{-1}$  for the unirradiated sample.  $\text{Ni}(\text{N}_3)_2$  and aged  $\text{Ni}(\text{OH})\text{N}_3$  are, however, not seriously affected even at high dosages of  $24\text{Mrad}$  of  $\gamma$ -radiation. Their reaction kinetics follow the unimolecular rate law just like those of unirradiated samples. Only the irradiation of  $\text{Ni}(\text{OH})\text{N}_3$  causes significant radiation damage. This work has shown that  $\text{Ni}(\text{OH})\text{N}_3$ , if carefully treated with calculated dosages of  $\gamma$ -radiation, could generate nickel azides of varying degree of stability for safe handling in various applications.

**KEY WORDS:** Pre-irradiation,  $\gamma$ -rays, azides, dislocations, radiation damage, thermal decomposition.

## INTRODUCTION

Most reactions of solids are susceptible to disturbing influences such as doping and pre-heating. Decomposition reactions of solid azides are most often influenced by lattice defects, pre-treatment of the sample by irradiation and heating. The doping of  $\text{Ba}(\text{N}_3)_2$  with  $\text{Na}^+$  or  $\text{Cr}^{3+}$  ions increases the decomposition rate without changing the activation energy, (Torker, 1968). The detonation characteristics of a mixture of lead azide and some monovalent azides as well as the role of polyvalent impurity atom,  $\text{M}^{n+}$  (whose chemical reaction produces detonation in inorganic primers) have been discussed (Zakarov, et al, 1975).

The effects of pre-irradiation (radiations ranging from UV to  $\gamma$ -rays) on the subsequent thermal decomposition of several azides have also been reported, (Thomas and Tompkins, 1951, Sood et. al, 1981). A drastic increase in decomposition rate and a decrease in the power law exponent have been observed by Prout and Moore (1966) for  $\text{Ba}(\text{N}_3)_2$  pre-irradiated with  $\gamma$ -rays. Investigations on ammonium perchlorate have also shown that exposure to radiation prior to thermal decomposition shortens the induction period and significantly increases the rate of

decomposition (Harley and Levy, 1973). Tompkins and young (1956) observed that pre-irradiation of barium styphnate does not however affect its rate of thermal decomposition.

Sood et al. (1982), studied the effect of UV radiation and pre-heating on the thermal decomposition of zinc azide and a small increase in the decomposition rates was observed. The results were interpreted in terms of induced defects at which points decomposition was preferred.

The aim of the present investigation is to find out the radiation damage caused by  $\gamma$ -radiation on samples of nickel(II) azide

## MATERIALS AND METHOD

### Materials

Anhydrous nickel (II) azide and nickel (II) hydroxy azide were obtained from analytical grade nickel (II) carbonate, sodium azide and 1:1 tetraoxosulphate (VI) acid and were used for the present investigation.

(i) Preparation of fresh anhydrous nickel azides:

Anhydrous nickel azide was prepared by distilling  $\text{HN}_3$  over  $\text{NiCO}_3$  followed by filtration and crystallization. The crystals were ground very mildly in a

dehumidified atmosphere (relative humidity < 60%) and stored in vacuum over  $P_2O_5$  for 30 days before the kinetic studies were performed. The nickel (II) azide was determined volumetrically with EDTA and Van de Mullen methods (Vande Mullen, 1961). It was found to have a composition of  $Ni(N_3)_2$ .

(ii) Preparation of  $Ni(OH)N_3$

It was prepared by first dehydrating nickel azide dihydrate,  $Ni(N_3)_2 \cdot 2H_2O$  crystals over  $P_2O_5$  and then exposing the normal nickel (II) azide to moist atmosphere (R.H>80%) for several days. The sample was thereafter mildly ground and stored in a vacuum of  $1.33 \times 10^{-3}$  mbars over  $P_2O_5$  for 30 days. The composition was established by EDTA and Van de Mullen methods to be  $Ni(OH)N_3$ .

Vande Mullen method of determining nitrogen involves the reaction of a nitrogen compound with excess of  $KMnO_4$  in the presence of  $H_2SO_4$ . The nitrogen generated in the reaction is estimated from the amount of  $KMnO_4$  that reacts with the compound by determining the excess amount of  $KMnO_4$  after reaction by titrating with standard KI. The iodine produced is estimated by reacting with 0.1M solution of sodium thiosulphite. This amount of iodine is equivalent to the excess  $KMnO_4$  which is subtracted from the total volume of  $KMnO_4$  to obtain amount that reacted with the nitrogen compound.

### Thermal decomposition of nickel (II) azides

In a decomposition run of pre-irradiated sample 1mg of each sample already irradiated in vacuum was weighed into the decomposition unit and then decomposed thermally at a fixed temperature of 515°K in the same manner as has already been described (Irom, 2002). The control of the temperature of decomposition was achieved within  $\pm 0.25^\circ C$  by connecting the vacuum system to a combination of,

- (i) dimmerstat for percentage transmittance,
- (ii) simmerstat for break and make contact and
- (iii) rheostat for regulating the input voltage or power.

The temperature of decomposition was recorded using a Pt-Pt/Rh 13% thermocouple with its tip at the centre of the furnace and connected to a portable potentiometer (CAM METRIC Ltd, Cambridge, England) through an ice bath. Thermal decomposition of nickel (II) hydroxy azide was also studied between 503° and 533°K.

## RESULTS AND DISCUSSION

### Thermal decomposition of fresh nickel (II) azide

Isothermal decomposition of fresh nickel azide,  $[Ni(N_3)_2]$ , pre-irradiated with  $\gamma$ -rays of 11.4Mrad and 20Mrad is compared with that of unirradiated sample studied at a constant temperature of 523K and the data are presented in table 1 and plotted in fig. 1. Stiochiometry of reaction is:

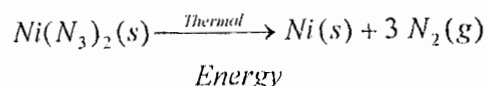


Figure 1 shows that the decomposition of Ni (II) azide starts immediately it is subjected to the decomposition temperature of 523°K and

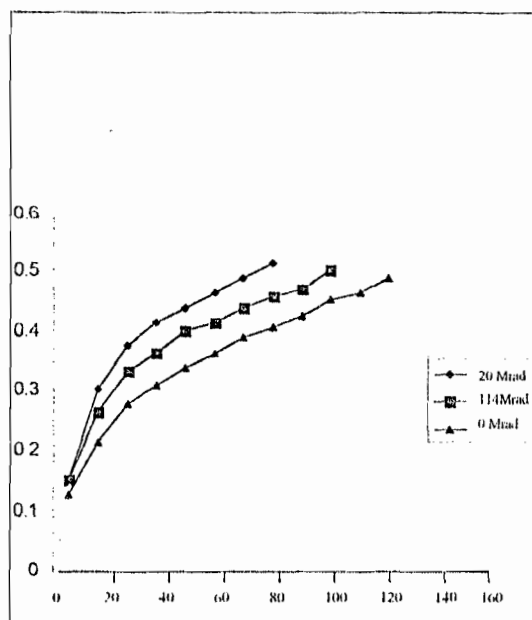


FIG. 1: THERMAL DECOMPOSITION OF NICKEL AZIDE,  $Ni(OH)N_3$ , PREIRRADIATED WITH DIFFERENT DOSAGES OF  $\gamma$ -RAYS AT 523K

the rate of production of  $N_2$  measured by  $\alpha = Pt/P_\infty$  progressively falls with time (fig.1). The  $\alpha$ -t curve could be split into two stages; an initial stage explained by the rate equation;

$$\text{Log}(1-\alpha) = C_1 - k_1 t$$

where  $k_1$  is a rate constant, for which a plot of  $\log(1-\alpha)$  vs  $t$  explains the initial stage ( $C_1 = 0$ ) and a final stage explained by the equation  $(1-(1-\alpha)^{1/3}) = k_2 t + C_2$  ( $k_2 =$  rate constant of final stage). Thus a plot of  $[1-(1-\alpha)^{1/3}]$  vs  $t$  explains the final stage for the decomposition of Ni (II) azide.

$\alpha =$  degree of decomposition given by  $\alpha = p_t/p_\infty$  where  $p_t$  is the pressure at any time,  $t$ , and  $p_\infty$  is pressure at infinite time, i.e. when the sample explodes

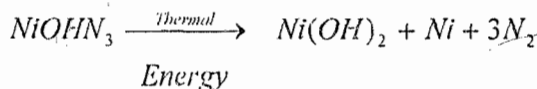
It is deduced from the curves that:

- (i) The rate constant,  $k$  of decomposition increases but only marginally. As seen in the shape of figure 1, the rates of decomposition in the graphs for the 20mrad and 11.4mrad are slightly higher than that for unirradiated sample (i.e, 0 rad).
- (ii) The activation energies in the two regions (exponential and contracting volume regions) increase very slightly from those of the unirradiated samples from  $147.15\text{KJ mole}^{-1}$  and  $82\text{KJ mole}^{-1}$  to  $150 \pm 2\text{KJ mole}^{-1}$  and  $84 \pm 3\text{KJ mole}^{-1}$  in the regions.
- (ii) There is hardly any effect of increase dosage of  $\gamma$ -radiation on the sample.

**Thermal decomposition of fresh nickel (II) hydroxy azide**

The fresh nickel hydroxy azide,  $Ni(OH)N_3$ , was pre-irradiated at a temperature of 513K with different dosages of 10Krad, 1mard, 5mrad, 10mrad and 20mrad. The reaction scheme is as follows:

$Ni(OH)_2$  was determined by EDTA titrimetry. Ni was determined by x-ray absorption method while nitrogen was determined



by gravimetric analysis of sample after decomposition was done. After determining  $Ni(OH)_2$  by titrating with 0.02M EDTA using murexide indicator, the total amount of  $Ni(OH)_2$  did not equate to the amount of decomposed sample. In calculating the stoichiometric weight of a possible product, Ni, the weight of sample and product were now balanced.

The presence of  $-OH$  was confirmed by physical means by running the I.R spectrum of product which gave a wave number of  $3600 \pm 4\text{cm}^{-1}$ . The presence of Ni was confirmed by x-ray fluorescence in which the absorption edge of Ni was obtained and compared with standards.

Table 2 gives the data for the thermal decomposition of nickel (II) hydroxy azide at 513K but pre-irradiated at different dosages. Figure 2 represents the curves for table 2, which generally shows an initial induction period preceded by an acceleratory region and finally the decay region. The shape is sigmoidal. Such decomposition pattern are explained by assuming that nucleation and nuclear growth depend on power law such that,

$$\alpha = kt^n \text{ or } \alpha = k(t \pm t_0)^n$$

where  $6 \geq n \geq 2$

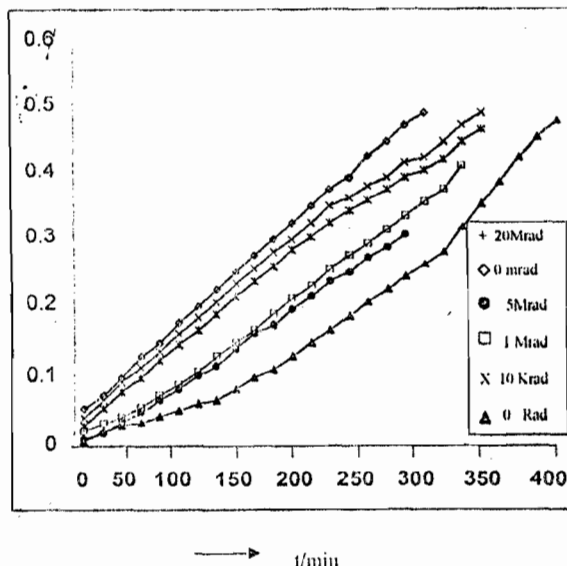


FIG. 2: THERMAL DECOMPOSITION OF  $Ni(OH)N_3$  PRE-IRRADIATED WITH DIFFERENT DOSAGES (TEMPERATURE: 513K)

**TABLE 1: THERMAL DECOMPOSITION OF NICKEL (II) AZIDE, PRE-IRRADIATED WITH DIFFERENT DOSAGES OF  $\gamma$ - RAYS AT 523k**

Time (mins)	$\alpha$ at different dosages		
	$^{20}$ Mrad	$^{11.4}$ Mrad	$^0$ rad.
10	0.15	0.15	0.125
20	0.300	0.262	0.212
30	0.375	0.331	0.275
40	0.412	0.362	0.306
50	0.437	0.400	0.337
60	0.462	0.412	0.362
70	0.487	0.437	0.387
80	0.512	0.456	0.406
90		0.468	0.425
100		0.500	0.450
110			0.462
120			0.487
130			
140			
150			

**TABLE 2: THERMAL DECOMPOSITION OF FRESH  $\text{Ni}(\text{OH})_2$  AT DIFFERENT DOSAGES AND 513K**

Time (mins)	$\alpha = P_t/P_{\infty}$ at different dosages					
	$^{20}$ Mrad	$^{10}$ Mrad	$^5$ Mrad	$^1$ Mrad	$^{10}$ Krad	$^0$ rad
10	0.050	0.037	0.025	0.019	0.006	0.003
20	0.069	0.062	0.050	0.028	0.016	0.019
30	0.094	0.087	0.075	0.037	0.030	0.025
40	0.125	0.109	0.094	0.053	0.043	0.031
50	0.144	0.131	0.119	0.069	0.062	0.038
60	0.172	0.156	0.141	0.084	0.078	0.047
70	0.194	0.178	0.162	0.103	0.097	0.057
80	0.219	0.200	0.184	0.125	0.112	0.062
90	0.244	0.228	0.209	0.144	0.134	0.078
100	0.269	0.250	0.231	0.162	0.156	0.094
110	0.294	0.275	0.253	0.184	0.169	0.106
120	0.319	0.294	0.278	0.206	0.191	0.125
130	0.344	0.319	0.297	0.225	0.209	0.144
140	0.369	0.344	0.319	0.247	0.231	0.162
150	0.387	0.356	0.337	0.269	0.244	0.181
160	0.422	0.375	0.353	0.287	0.266	0.200
170	0.444	0.387	0.369	0.309	0.281	0.219
180	0.469	0.412	0.387	0.328	0.300	0.237
190	0.487	0.419	0.400	0.350		0.256
200		0.444	0.416	0.369		0.275
220		0.469	0.444	0.406		0.312
240		0.487	0.462			0.347
260						0.381
280						0.419
300						0.450
320						0.475
340						
360						

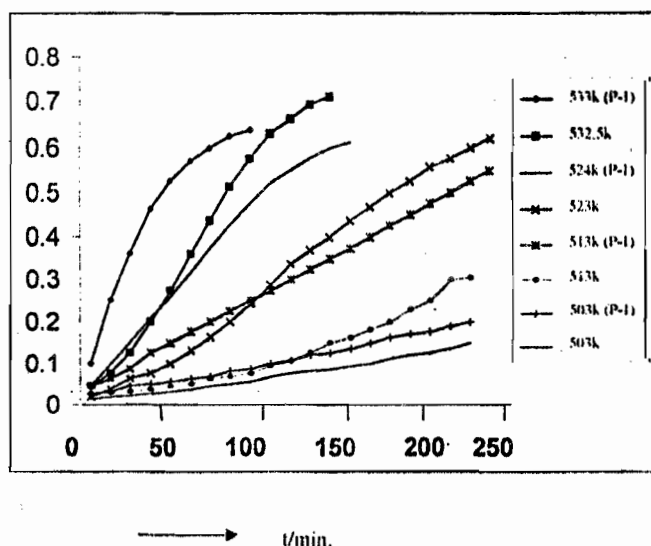


FIG. 3: THERMAL DECOMPOSITION OF Ni(OH)N<sub>3</sub> AT DIFFERENT TEMPERATURES (DOSAGE: 20 MRAD)

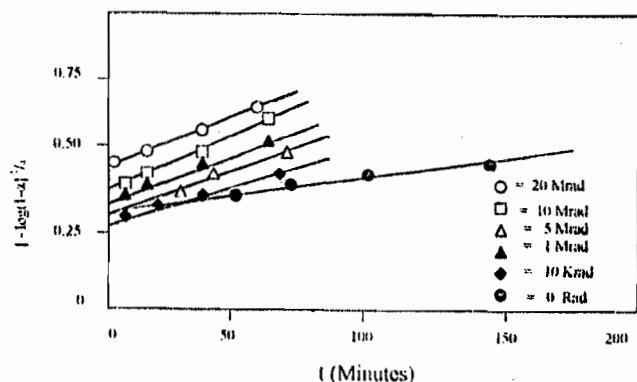


FIG. 4: The Avrami Erofeev Plots for the unirradiated and the Pre-irradiated Ni(OH)N<sub>3</sub> Different dosages and constant temperature, 513°K.

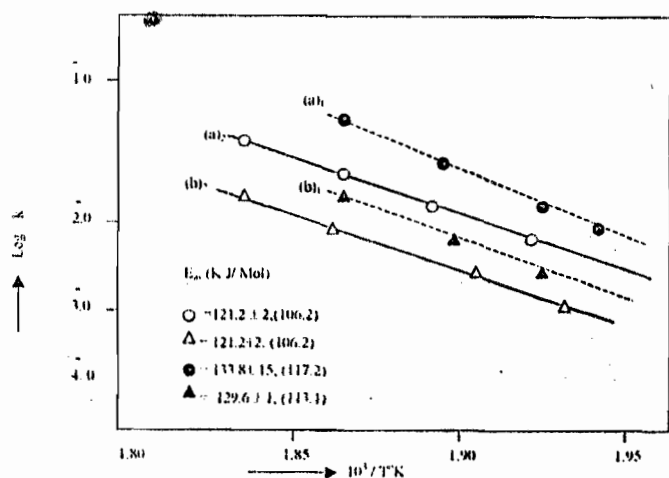


FIG. 5: Arrhenius plot of (a) the Avrami-Erofeev and (b) the contracting cube rate constants of the unirradiated (-) and Pre-irradiated (10 Krad to 20 Mrad) Ni(OH)N<sub>3</sub>

and  $t_0$  is the induction period.

This represents the acceleratory region which is explained by applying the Avrami-Erofeev equation,  $-\log(1-\alpha) = kt^n$ .

Fig. 3 is a plot of data in table 3, which is the decomposition of Ni(II) hydroxy azide at a temperature range of 503k to 533k but pre-irradiated at a fixed dosage of 20Mrad. A plot of  $-\log(1-\alpha)^{1/4}$  vs  $t$  is represented in fig. 5 and the rate constants,  $k$  at different temperatures plotted against  $1/T$  are used to calculate the activation energy for the acceleratory region in fig. 5.

The decay region is explained using the contracting envelope law,  $(1-(1-\alpha)^{1/3}) = k_2t + C$  and activation energy for this region is obtained again by plotting  $k_2$  vs  $1/T$  using Arrhenius equation.

Thus from the curves in figs. 2 and 3 it is found that:

- i) The rate constants increase substantially in the initial and final stages at all temperatures.
- ii) The acceleratory period is shortened and induction period reduced with increasing dosage.
- iii) The energies of activation in both the acceleratory and the decay regions increase from 106.2KJ mole<sup>-1</sup> for the unirradiated to 117.8KJ mole<sup>-1</sup> (fig. 5).

### Thermal Decomposition of aged nickel (II) hydroxy azide

The thermal decomposition of aged nickel hydroxy azide, ground mildly and then pre-irradiated respectively with 10krad, 5mrad and 24mrad of  $\gamma$ -radiation was studied. The sample irradiated with 24mrad, on subsequent thermal decomposition follows the same kinetics and the same energy of activation as Ni(II) azide ( $\gamma$ -radiation of 24mrad is used for this purpose as it is considered high enough to cause serious radiation damage which will necessarily affect the activation energy of thermal decomposition of the sample). Increased dosage in this case is also accompanied by saturation in the rate constant values of decomposition, though these values in both the exponential and contracting cube regions



TABLE 4: THERMAL DECOMPOSITION OF AGED Ni(OH)N<sub>3</sub> PRE-IRRADIATED WITH DIFFERENT DOSAGES AT 508K

Time (min)	$\alpha = P_t/P_\infty$ at different irradiation Dosages				
	<sup>60</sup> 24K Mrad	<sup>60</sup> 5 Mrad	<sup>60</sup> 0.5Mrad	<sup>60</sup> 0.5mrad	<sup>60</sup> 1.0K rad
10	0.081	0.037	0.056	0.056	0.047
20	0.125	0.112	0.100	0.100	0.091
30	0.169	0.156	0.144	0.137	0.131
40	0.212	0.194	0.175	0.171	0.169
50	0.244	0.231	0.212	0.206	0.200
60	0.278	0.262	0.244	0.237	0.228
70	0.312	0.290	0.269	0.262	0.256
80	0.337	0.322	0.294	0.287	0.275
90	0.355	0.337	0.312	0.306	0.297
100	0.387	0.356	0.331	0.316	0.312
110	0.406	0.369	0.344	0.337	0.331
120	0.419	0.387	0.362	0.350	0.344
130	0.437	0.397	0.375	0.362	0.356
140		0.406	0.387	0.375	0.369
150		0.419	0.400	0.387	0.381
160		0.431	0.412	0.397	
170			0.425	0.412	
180			0.437	0.419	
190					
200					

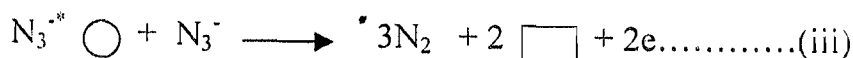
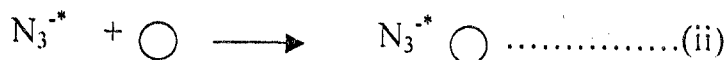
TABLE 5 :COMPARATIVE KINETIC PARAMETERS OF THERMAL DECOMPOSITION

Parameter considered	Ni(II) Azide	Ni(II) hydroxy azide	Aged Ni(II) hydroxy azide
1. Characteristics of curves	Curves show continuous deceleration from onset of decomposition	Decomposition curves are sigmoidal at low irradiation at all temperatures, and similar to the unirradiated decomposition	Slow decomposition behavior similar to Ni(II) azide
2. Effect of increased $\gamma$ -radiation dosage	Pre-irradiation only slightly affect the constants of decomposition at all dosages considered	At high irradiation the rate constants for the acceleratory region increase tending towards continuous deceleration as in Ni(II) azide	Same as Ni(II) azide
3. Activation energy	Changes marginally from 147 and 82Kj mol <sup>-1</sup> to 150 and 84KJ mol <sup>-1</sup> for the two regions of decomposition	Values for the two regions change from 106KJ mol <sup>-1</sup> for the unirradiated azide to 117KJ mol <sup>-1</sup> for sample pre-irradiated at 20mrad.	Effect is the same as for Ni(II) azide

Note: Activation energy was obtained using the Arrhenius expression,

**DISCUSSION**

The reaction scheme for the decomposition of Ni(II) azide is as shown below (Sood et al, 1981).



According to them the primary process of the decomposition is the formation of exciton,  $N_3^*$  and the decomposition is between  $N_3^*$  trapped at a suitable site, eg a cationic vacancy, O, and an adjacent azide ion (equation iii). This process results in the production of  $N_2$ , 2 anionic vacancies and metallic Ni. For the Ni (II) hydroxy azide, the scheme is basically the same, except for the production of Ni (II) hydroxide which reduces the extinction coefficient of the thermal energy. The thermal decomposition kinetics of Ni (II) hydroxy azide at low irradiations show induction and acceleratory periods. The presence of -OH ions thus results in the time-dependent decomposition of the azide. The above observations show that the decomposition characteristics of only nickel (II) hydroxy azide are affected markedly by pre-irradiation with  $\gamma$ -rays whereas the other two samples remain almost unaffected.

As with ammonium perchlorate (Harley and Levy, 1973), in the case of the Avrami-Erofeev kinetics which are also applicable to  $Ni(OH)N_3$  the radiation effects enumerated above can be attributed to an increase in nucleation rate, the number of decomposition nuclei or to a combination of both the possibilities. Initially radiation will produce nitrogen at both internal and external surfaces and at imperfections such as F-Centres and dislocations (figure 7).

Further irradiation will then probably cause decomposition at normal lattice sites with build-up of nitrogen internally. This gas will diffuse into pockets causing rupture and further decomposition at newly formed sites. When this process has proceeded to some extent, sufficient gas, produced within the lattice, accumulates in the voids created by irradiation and exert enough stress on the lattice to cause the generation of dislocations. These new dislocation become additional decomposition nuclei giving rise to increased Avrami-Erofeev rate constants of pre-irradiated nickel hydroxy azide.

The decrease in acceleratory period and the inflexion points of the decomposition of samples with increasing dosage and a poor fit of the  $\alpha$ -t data in the acceleratory region beyond 5mrad irradiation (fig. 2) indicates the possibility of fracture of the crystals under heavy irradiation of between 10mrad and 20mrad thereby exposing a fresh surface of the material to the process of fast nucleation.

As mentioned earlier irradiation of nickel (II) azide and aged nickel (II)

hydroxyazide with varying dosages of  $\gamma$ -radiation has little or no effect on the thermal decomposition data which could also be described by the unimolecular nucleation as it is with the unirradiated samples (figures 1 and 6). Irradiation of  $[Ni(OH)N_3]$  however causes serious radiation damage resulting in the gradual removal of the induction and decrease in the acceleratory periods of its kinetics as the radiation dosage increase (fig.2). The irradiation progressively removes the time-dependence of nucleation noticed in the unirradiated sample and at heavy irradiation a unimolecular nucleation appropriately describes the decomposition. The increased activation energy of 117KJ mole<sup>-1</sup> in both regions could, however, be due to the fracture of  $[Ni(OH)N_3]$  at heavy irradiation.

Mild mechanical deformation of aged  $[Ni(OH)N_3]$  completely removes the time-dependence of nucleation and the ground material decomposes according to unimolecular decay law. These observations combined together prove that pre-irradiation and grinding have the same effect on nickel hydroxy azide. It has already been suggested that ageing of fresh nickel hydroxy azide seems to transform it into fresh nickel azide which decomposes by a unimolecular law

Harley and Levy (1973), by employing etch pit technique on ammonium perchlorate exposed to  $\gamma$ -rays or x-rays, have identified dislocations as the radiation-induced decomposition nuclei. They have suggested that the role of irradiation is to produce decomposition at preferred sites such as internal defects.

(Irom, 2002). Obviously one could reconstruct the fresh material from the aged sample either by pre-treatment or grinding. The alpha lead azide (Jack, 1963), mercury fulminate (Bartlett, et al, 1956) and silver oxalate (Finch et. al, 1954) are other compounds which can be similarly reconstructed through pre-treatment.

## CONCLUSION

Pre-irradiation of the three samples of nickel azide causes noticeable radiation damage in only  $[Ni(OH)N_3]$ , the fresh nickel hydroxy azide, while nickel (II) azide and aged nickel (II) hydroxy azide are only marginally affected by the operation. These conclusions could be derived from the kinetic data on the thermal decomposition of nickel (II) azide.



Thermal decomposition of Aged  $\text{Ni}(\text{OH})\text{N}_3$ , like that of  $[\text{Ni}(\text{N}_3)]$  shows rates which do not differ significantly from that of the unirradiated azide at all dosages of pre-irradiation. The decomposition which takes place by the unimolecular nucleation law points to the high instability of these samples.

However thermal decomposition of nickel (II) hydroxy azide shows significant change in decomposition rate as the radiation dosage increases. The significant change from time-dependent nucleation for the unirradiated azide to unimolecular nucleation of the heavily irradiated sample points to the possibility of radiation damage caused by  $\gamma$ -radiation thus making the azide more sensitive to thermal radiation.

It has already been reported that the substitution of one  $\text{OH}^-$  in  $\text{Ni}(\text{N}_3)_2$  for  $\text{N}_3^-$  desensitizes the azide, which implies that  $\text{Ni}(\text{OH})\text{N}_3$  is more stable to effects of radiation, shock or impact than  $\text{Ni}(\text{N}_3)_2$  (Irom, 2002).

Pre-irradiation of  $\text{Ni}(\text{OH})\text{N}_3$  removes the time-dependence of nucleation resulting in its decomposition according to the unimolecular decay law. Pre-irradiation therefore transforms the otherwise stable  $\text{Ni}(\text{OH})\text{N}_3$  to an unstable  $\text{Ni}(\text{N}_3)_2$ . We can harness this result for improved and safe use of  $\text{Ni}(\text{N}_3)_2$  which itself is dangerously explosive to handle.

Pre-treatment of materials, in this case, has become a veritable technological operation employed by material scientists to alter the properties of substances towards targeted applications. As has already been reported  $\text{Ni}(\text{OH})\text{N}_3$  is more stable than  $\text{Ni}(\text{N}_3)_2$  (Irom, 2002). Therefore, in areas of application such as mining, which require powerful explosives,  $\text{Ni}(\text{OH})\text{N}_3$  could be treated by pre-irradiation with calculated dosages of  $\gamma$ -rays in order to activate the azide to the desired explosive. This treatment is therefore recommended for the construction of explosives for different applications.

## RECOMMENDATIONS

Further studies should be conducted to determine the nature of thermal decomposition, whether endo or exothermic reaction, by conducting DTA studies on pre-irradiated azides. Kubiak (1982) has already conducted DTA studies of  $\text{Ni}(\text{II})$  azide and reported that decomposition which is

exothermic starts as soon as the sample is raised to the decomposition temperature. Furthermore the decomposition temperatures of the azides should be determined using thermogravimetric techniques.

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