THERMAL DECOMPOSITION OF NICKEL AZIDE

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The results on the thermal decomposition of anhydrous nickel azide prepared by reacting nickel azide solution with AnalaR Me_2CO are reported in the temperature range 490–525 K. The sample starts to decompose immediately after it is raised to the decomposition temperature and the rate of decomposition continuously decreases.

The decomposition kinetics have been explained in terms of exponential decay law for $\alpha \simeq 0.19$ and contracting volume law for $\alpha > 0.19$. The domain of exponential decay law corresponds to the initial decomposition pertaining to surface nucleation and two dimensional surface growth of the product phase, while contracting volume law explains the growth of the product phase into the bulk. The role of defects has been explained by electrical conduction studies on the sample.

Thermal decomposition of the transitional metal azides has been studied to a considerable extent in case of d^9 and d^{10} [1, 2] elements, while those of d^5 to d^8 have not been attended to. Recently, the relative stabilities of $Cu(N_3)_2$ and other divalent azides has been explained in terms of the order of the lattice symmetry and an azide having low order of symmetry is very sensitive to explosion. $Ni(N_3)_2$, an azide of $3d^5$ element, has been reported as a highly sensitive explosive azide [3] but no studies have been made to relate its explosiveness to lattice symmetry, electronic properties such as band-gap, ionization potential and metal-azide bond. The thermal decomposition of nickel azide has not been reported in the past and as part of studies of the decomposition of nickel azide we now report the results on its thermal decomposition. The results on photolysis of nickel azide have already been communicated.

Experimental

Nickel azide was prepared by distillation of HN_3 onto a suspension of nickel carbonate followed by filtration to remove insoluble material. The solution was treated with an excess of AnalaR grade acetone.

A sandy green precipitate thus obtained was filtered and dried over fused calcium chloride in vacuum. Volumetry analysis by the method discussed by Taylor established the composition to be $Ni(N_3)_2$.

Thermal decomposition was carried out at 10^{-6} Torr in an isolated low pressure unit (Fig. 1a). The decomposition cell (Fig. 1b) consisted of a long tube and was connected to a winch on top by means of B-24 quick fit joint. The winch was used for raising the bucket containing the sample to the decomposition chamber. An
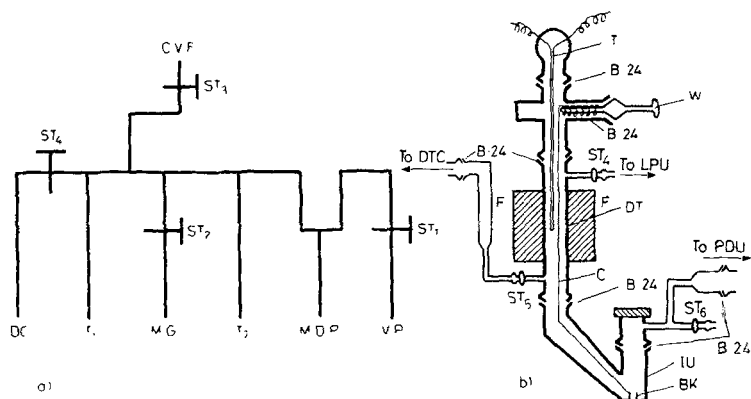
Fig. 1a. Low pressure unit diagram: DC = Decomposition cell; ST, ST_2, ST_3, ST_4 = High vacuum stop cocks; T_1, T_2 = Traps; C.V.F. = Constant volume flask; M.D.P. = Mercury diffusion pump; V.P. = Vacuum pump; M.G. = McLeod gauge

Fig. 1b. Decomposition unit: DT = Decomposition tube; T = Thermocouple; ST_4, ST_5, ST_6 = High vacuum stop cocks; W = Winch arrangement; B.24 = Standard quick fit joints; F = Furnace; Q = Quartz disc; BK = Sample bucket; IU = Irradiation unit; PDC = Photo decomposition cell; DTC = Differential thermal cell; LPU = Low pressure unit; C = Thin copper wire
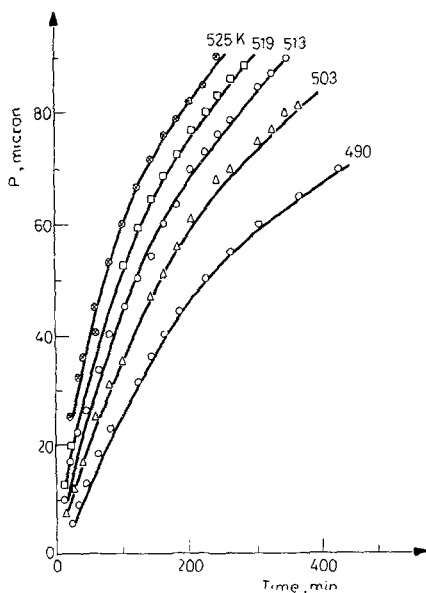

Fig. 2. Decomposition of nickel azide at various temperatures: ○ = dec. at 490 K; △ = dec. at 543 K; ⊕ = dec. at 513 K; □ = dec. at 519 K; ⊕ = 525 K

irradiation chamber was attached at the bottom of the long tube by means of another B-24 quick fit joint. A quartz window was sealed at the open mouth of the irradiation chamber by means of piecene wax. A Pt-PtRh 13% thermocouple with its tip at the centre of the furnace was used to note the temperature of decomposition. The decomposition cell was connected to the differential thermal and the photo cell according to Fig. 1b. In a typical decomposition kinetic study, one mg of the anhydrous azide was accurately weighed and evacuated for twenty four hours at 10^{-6} Torr. Subsequently the furnace enclosing the decomposition chamber was raised to the desired temperature, the degassing rate of the system recorded and the system was once again evacuated for two hours. The bucket containing sample was raised very near to the thermocouple tip in the decomposition chamber.

A McLeod gauge was used to record the pressure of nitrogen produced due to azide decomposition. The values of pressure were corrected for the rate of degassing before being fitted into any rate equation. The same procedure was followed in case of preirradiated sample.

Results and discussion

A freshly prepared sample of $Ni(N_3)_2$ was aged over fused $CaCl_2$ for thirty days in vacuum of 10^{-2} Torr at 25°. No attempt was made to study the effect of ageing on the kinetics of decomposition. The thermal decomposition of $Ni(N_3)_2$ has been studied in the temperature range $490-525$ K and the results are summarized below.

1. $Ni(N_3)_2$ starts to decompose immediately after it is raised to the decomposition temperature. The rate of evolution of N_2 due to azide decomposition progressively decreases with time (Fig. 2). No acceleratory period is observed at any stage of decomposition.

2. The thermal decomposition of $Ni(N_3)_2$ does not go to completion and after about 35% of the decomposition, the rate becomes negligibly small.

3. The $\alpha - t$ curves could not be fitted into any single rate equation necessitating, thereby, a split of each $\alpha - t$ curve into initial and final stages of decomposition. $\log (1 - \alpha)$ vs t explains the initial stages of decomposition corresponding to $\alpha \simeq 0.19$

$$\therefore \log (1 - \alpha) = C_1 - K_1 t$$

where K_1 is the rate constant explains the initial stages of decomposition. For $\alpha > 0.19$ contracing volume law;

$$(1 - (1 - \alpha)^{\frac{1}{3}}) = K_2 t + C_2$$

where K_2 is the rate constant explains the decomposition kinetics.

The plots for exponential decay law and contracting volume law are respectively represented in Figs (3) and (4). The energies of activation in the initial and final domains of decomposition are 88.8 and 70.3 kJ/mole, respectively.
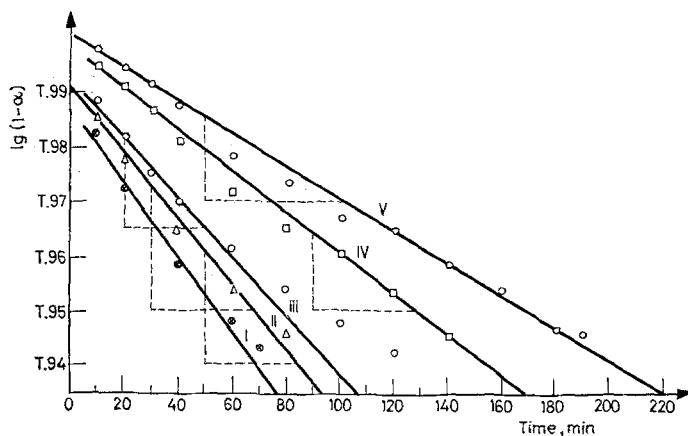
Fig. 3. Graph of log $(1 - \alpha)$ vs. time
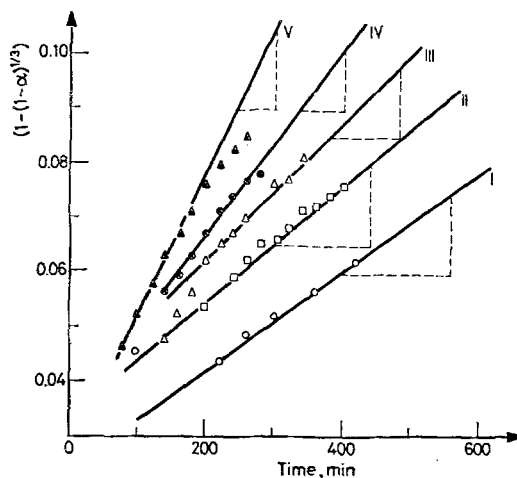
Fig. 4. Graph of $(1 - (1 - \alpha)^{1/3})$ vs. time

4. No attempt was made to record the pressure of N_2 during the first ten minutes of decomposition due to the non-attainment of the decomposition temperature by the sample.

The fast initial decomposition whose rate progressively decreases with time has also been observed in the case of NaN_3 [5], $Zn(N_3)_2$ [6], NH_4ClO_4 [7] and lead chromate [8]. The initial fast decomposition is too high to be accounted for surface desorption and has been explained in terms of surface decomposition of the azide in the case of the azides of sodium and zinc. The general interpretation of the $\alpha - t$ curves of the type shown in Fig. 2 would then be that during the short interval of time in which the azide platelets are raised to the decomposition temperature, nucleation sets in instantaneously on all surfaces. Nuclei can now grow in

all the three dimensions but if we assume and the surface growth is much faster than the growth into the bulk, the platelets surface will be covered with the product layer in a very short time. During this time a small penetration of the product phase into the bulk of the platelets is also possible and the thickness of the product phase may be a few molecular layers. The picture then becomes a random nucleation with three dimensional anisotropic growth for which the Erofeev's equation can be solved to the form

$$\alpha = 1 - \exp(-Kt)$$

where K is the rate constant. Such a solution of this equation has been reported for $Zn(N_3)_2$ decomposition [6]. The energy of activation obtained from the plot of the rate constant of exponential decay reaction at different temperatures vs $\frac{1}{T}$, is therefore utilized for the nucleation process as well as for the growth mostly on the surface.

The exponential decay reaction is succeeded by contracting volume reaction and corresponds to the region $\alpha > 0.19$. Since the value of α corresponding to the onset of the contracting volume reaction is very small it can be concluded that nuclei are formed in areas of highest defect densities and there is a considerable overlap of the growing nuclei even at low degrees of decomposition. The energy of activation obtained from the exponential decay law is used mostly for the process of nucleation and a small fraction of it should be associated with rapid two dimensional surface growth and nuclei overlap. Defect structure where nucleation is favoured are high defect order corresponding to dislocation and grain boundaries as described by Mitchell for AgBr [9]. It is true to say, however, that the surface reaction is more important in the initial stages of $Ni(N_3)_2$ decomposition. The penetration inwards, into the azide platelets of these interfering growth nuclei will constitute contracting volume reaction as described in Fig. 4. The energy of activation in this region is used only for the inward growth of these nuclei.

Thermal decomposition of preirradiated nickel azide

The results on the kinetics of subsequent thermal decomposition of $Ni(N_3)_2$ irradiated with ultra violet light for 10 minutes could be fitted only into contracting volume expression. The source of ultra violet light was an HPK 125 (80 W) Hg lamp which has a strong emission at 2537 Å. In order to obtain maximum intensity no filters were employed. During the irradiation itself the evolution of a considerable amount of N_2 is noticed. The rate of thermal decomposition of the preirradiated sample is higher than that of the corresponding unirradiated sample. The effect of preirradiation can be explained in terms of defects at which the reaction is preferred and also by the mechanical strain imposed by the irradiation products. During preirradiation there is a very rapid nucleation at the energetically favoured positions on the surface or on the internal grain boundaries. Since there is no observable initial decomposition in the case of the preirradiated sample, it
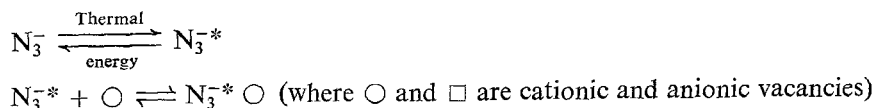
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is assumed that the nucleation during the process of preirradiation is very rapid followed by a considerable overlap of the growing nuclei leading to the complete coverage of the surface of the platelets. The subsequent thermal decomposition of the sample should then follow the contracting volume expression which has been experimentally observed. No attempt was made to study the thermal decomposition at a temperature after irradiation for different dosages so the effect of preirradiation on activation energy can not be concluded.
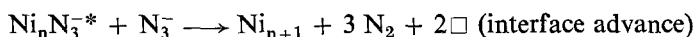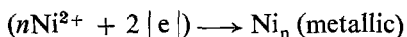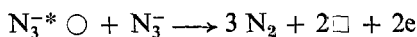
Mechanism of decomposition

The applicability of the exponential decay law during the initial stages of decomposition shows that the initial decomposition takes place at those centres which are consumed rapidly during the course of decomposition. The energy of activation for temperature dependence electrical conductivity in the temperature range $303-415$ K for nickel azide [10] is 13.5 kJ/mol and this shows that Frenkel defects play a definite role in the decomposition process. The appreciable difference in the ionic radii of the ions concerned should also favour Frenkel defect structure. The initial reaction of nickel azide decomposition can be explained from its conductivity results. Like KCl or KN_3, nickel azide is probably a cationic conductor at temperatures below 415 K. In the high temperature region the energy of activation increases very sharply and the conductivity may be ionic. During the initial decomposition process anionic vacancies are produced which penetrate into the interior of the micro crystals so that the fresh layers of the azide are consumed until probably the whole azide decomposes. During later stages of decomposition, the migration of nickel ions and nickel atoms play a significant role in the growth of the metal nuclei or in the advance of $Ni/Ni(N_3)_2$ interface.

At the end of the domain of the exponential decay law, we can imagine metallic nickel to be in the form of thin layers at grain boundaries and as compact nuclei at junctions of grains similar to the observations of Secco [11]. Larger nuclei can be formed by simple aggregation of mobile nickel atoms. The result would be that individual microcrystals become rapidly covered with a thin layer of metallic nickel. The next stage of decomposition would be the penetration of the envelope into the interior of the microcrystals by movement of the $Ni/Ni(N_3)_2$ interface.

During photolysis and photoconduction [10] studies of $Ni(N_3)_2$ it has been reported that the primary process of decomposition is the formation of exciton and the decomposition is between an exciton trapped at a suitable site during the life time of the exciton with an adjacent azide ion in the immediate neighbourhood. The sequence of the reactions, explaining the decomposition will then be

$$N_3^- \underset{energy}{\overset{Thermal}{\rightleftharpoons}} N_3^{-*}$$

$N_3^{-*} + \bigcirc \rightleftharpoons N_3^{-*} \bigcirc$ (where $\bigcirc$ and $\square$ are cationic and anionic vacancies)

$$N_3^- {}^* \bigcirc + N_3^- \longrightarrow 3 N_2 + 2\square + 2e$$

$$(n Ni^{2+} + 2 \, | \, e \, |) \longrightarrow Ni_n \text{ (metallic)}$$

$$Ni_n N_3^- {}^* + N_3^- \longrightarrow Ni_{n+1} + 3 N_2 + 2\square \text{ (interface advance)}$$

The reaction later advances at $Ni/Ni(N_3)_2$ interface. The decomposition of $Ni(N_3)_2$ is similar to that of $Zn(N_3)_2$ with the only difference that $Ni(N_3)_2$ decomposes faster and is more explosive. An attempt to study the decomposition of $Ni(N_3)_2$ at around 540 K results in explosion but $Zn(N_3)_2$ decomposes very fast without an explosion.

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ZUSAMMENFASSUNG — Die Ergebnisse der thermischen Zersetzung von aus einer Nickel-azid-Lösung mit AnalaR Me_2CO hergestelltem wasserfreiem Nickelazid im Temperaturbereich 490—525 K werden beschrieben. Die Zersetzung der Probe beginnt sofort nach dem Erreichen der Zersetzungstemperatur und die Zersetzungsgeschwindigkeit nimmt ständig ab.

Die Zersetzungskinetik wurde auf der Grundlage des exponentiellen Zerfallsgesetzes für $\alpha \simeq 0.19$ und des Volumenkontraktionsgesetzes für $\alpha > 0.19$ erklärt. Das Gebiet des exponentiellen Zerfallsgesetzes entspricht der anfänglichen Zersetzung, welche mit der Oberflächenkeimbildung und dem zweidimensionalen Oberflächenwachstum der Produktphase verbunden ist, während das Volumenkontraktionsgesetz das Wachstum der Produktphase innerhalb der Probe erklärt. Die Rolle der Defekte wurde durch elektrische Leitfähigkeitsuntersuchungen an der Probe erklärt.

Резюме — Приведены результаты термического разложения в области температур 490—525 K безводного азида никеля, полученного при реакции раствора азида никеля с АналаR. Me_2CO. Образец начинает разлагаться сразу же после достижения температуры разложения и скорость разложения непрерывно уменьшается. Кинетика реакции разложения была объяснена на основе закона экспоненциального затухания с $\alpha > 0.19$ и закона сжатых объемов для $\alpha > 0.19$. Область закона экспоненциального затухания соответствует начальному разложению приводящему к образованию центров кристаллизации на поверхности и двумерный поверхностный рост новой фазы. Закон сжатых объемов объясняет рост новой фазы во всем объеме. Роль дефектов объяснена исходя из измерений электропроводности образца.