

# Influence of Linear Flow Velocity of Uncracked Ammonia (NH<sub>3</sub>) Gas on Formation of Higher Nitrides, $\delta$ -MoN and $\epsilon$ -Fe<sub>2</sub>N, under Concentrated Solar Irradiation in the SF40 Solar Furnace at PSA

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**Abstract** Nitriding experiments for powder specimens of Mo and Fe were carried out using a solar furnace SF40 at PSA (Plataforma Solar de Almería) in Tabernas (Spain) in uncracked ammonia NH<sub>3</sub> gas (NH<sub>3</sub> gas with suppressed extent of dissociation by flowing) aiming at determining the range of linear velocity  $v$  of NH<sub>3</sub> gas flow to yield higher nitride phases,  $\delta$ -MoN for Mo and  $\epsilon$ -Fe<sub>2</sub>N for Fe. Standard solar exposure duration at a specified reaction temperature  $T$  was set to be 60 min over range of  $v$  between 1.14 mm·s<sup>-1</sup> and 11.4 mm·s<sup>-1</sup>. By X-ray diffraction (XRD) analysis, presence of  $\delta$ -MoN was detected besides  $\gamma$ -Mo<sub>2</sub>N and metallic Mo for Mo powder specimen heated to 900 °C in NH<sub>3</sub> gas flow at  $v = 1.14$  mm·s<sup>-1</sup> but XRD peaks identifiable as  $\delta$ -MoN became indiscernible when  $v$  was increased to 11.4 mm·s<sup>-1</sup>. On the other hand, for Fe powder specimen exposed to NH<sub>3</sub> gas flow at  $v = 1.14$  mm·s<sup>-1</sup> at  $T = 500$  °C, remnant metallic  $\alpha$ -Fe was detectable by XRD at the down-stream side of the specimen holder but no metallic  $\alpha$ -Fe was detected at the up-stream side of the specimen holder suggesting that chemical activity  $a(N)$  of N atom in uncracked NH<sub>3</sub> gas tended to decrease along the NH<sub>3</sub> gas flow path on going from the up-stream side to the down-stream side.

**Keywords** Uncracked ammonia (NH<sub>3</sub>) gas, Concentrated solar energy, Temperature homogenizer,  $\delta$ -MoN,  $\epsilon$ -Fe<sub>2</sub>N

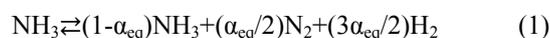
## 1. Introduction

On account of unique properties of nitrides of transition metals, intensive research efforts have been invested for nitride synthesis. Besides high hardness of metal nitride MN, some MN's are claimed to possess special functional properties. For example, Inumaru et al. [1] investigated aspects of high-pressure synthesis of  $\delta$ -MoN in view of  $\delta$ -MoN being a superconducting material. On the other hand,  $\epsilon$ -Fe<sub>2</sub>N appears to be considered as a promising candidate material for anode in lithium ion battery [2, 3].

Generally, synthesis of nitride MN through reaction of metal M in N<sub>2</sub> gas atmosphere requires high temperature due to high chemical stability of N<sub>2</sub> gas molecules.

Synthesis of "higher" nitride such as  $\delta$ -MoN of Mo cannot be realized in N<sub>2</sub> gas environment even at very high N<sub>2</sub> gas partial pressure  $p(N_2)$  of order of several hundreds of atm for prolonged reaction duration of several tens of hours [1, 4-16].

One of optional routes for synthesizing higher nitride of metal M by reaction at normal pressure is the use of uncracked NH<sub>3</sub> gas as a powerful nitriding medium [4, 5, 7, 8, 10-22]. Uncracked NH<sub>3</sub> is a stream of NH<sub>3</sub> gas whose degree  $\alpha$  of dissociation is suppressed from the degree of dissociation  $\alpha_{eq}$  under equilibrium state in a closed reaction chamber



Inherently unstable nature of uncracked NH<sub>3</sub> gas leads to the following two characteristic features on its usage as a nitriding medium;

<1> at a specified spot in the reactor set at temperature  $T$ , extent  $\alpha$  of dissociation of uncracked NH<sub>3</sub> is determined as a function of its linear flow velocity  $v$ ,

<2> along the NH<sub>3</sub> gas flow path at any given  $T$ ,  $\alpha$  would

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increase steadily on going from up-stream side to down-stream side.

That is, nitriding power of uncracked NH<sub>3</sub> gas determined by the chemical activity  $a(\text{N})$  of uncracked NH<sub>3</sub> gas molecule tends to decrease with decreasing  $v$  at a given  $T$  and, even at given  $v$  and  $T$ ,  $a(\text{N})$  of uncracked NH<sub>3</sub> gas tends to decrease along the flow path on going from up-stream side to down-stream side on account of increasing  $\alpha$  (i.e. decreasing partial pressure  $p(\text{NH}_3)$  of NH<sub>3</sub> gas). In other words, even at given experimental conditions of  $T$  and  $v$ ,  $a(\text{N})$  of uncracked NH<sub>3</sub> gas would decrease steadily along the flow path on going from inlet side to outlet side of the reaction tube. This trend was experimentally demonstrated by Nishimaki *et al.* [14] as decreasing N content in hypo-stoichiometric  $\epsilon$ -Fe<sub>2</sub>N phase synthesized in NH<sub>3</sub> gas stream at 550 °C along the flow path over about 4 cm length. In the preceding works using uncracked NH<sub>3</sub> gas as a nitriding medium under irradiation of concentrated solar beam, synthesis of nitride MN was detected for transition metals including Ti, Zr, V, Nb, Ta, Cr, Mo and W and also for Fe [7, 8, 21, 23]. However, these results were obtained using a spherical reactor made of Pyrex glass in which NH<sub>3</sub> gas flow pattern was unknown. In these preliminary works of nitriding group of transition metals in stream of NH<sub>3</sub> gas, metal specimens were in form of compacted pellet in order to carry out the test runs with minimized risk of cross-contamination among specimen materials within the limit of designated solar beam time for users.

In the recent experimental campaign carried out in September/October 2017 at PSA using SF40 for nitriding Mo and Fe powder specimens, specially designed tubular silica glass furnace and steel specimen holder were used to look into influences of  $v$  of NH<sub>3</sub> gas stream and of specimen position along the NH<sub>3</sub> gas flow path on phases synthesized. Range of linear NH<sub>3</sub> gas flow velocity  $v$  tested was between 1.14 and 11.4 mm·s<sup>-1</sup> that corresponded to volumetric flow rate of 0.08 and 0.83 L·min<sup>-1</sup>, respectively, in the used experimental setup. Steel specimen holder was drilled with 4 holes of diameter 8 mm and depth 5 mm to hold powder specimens of Mo or Fe and these 4 holes were designated with P1 at up-stream side of NH<sub>3</sub> gas stream to P4 at down-stream side. The distance between the central spot of P1 and the central spot of P4 was 45 mm.

Test results acquired for nitride synthesis for Mo and Fe in stream of NH<sub>3</sub> gas under irradiation of concentrated solar beam are summarized in this report.

## 2. Experimental

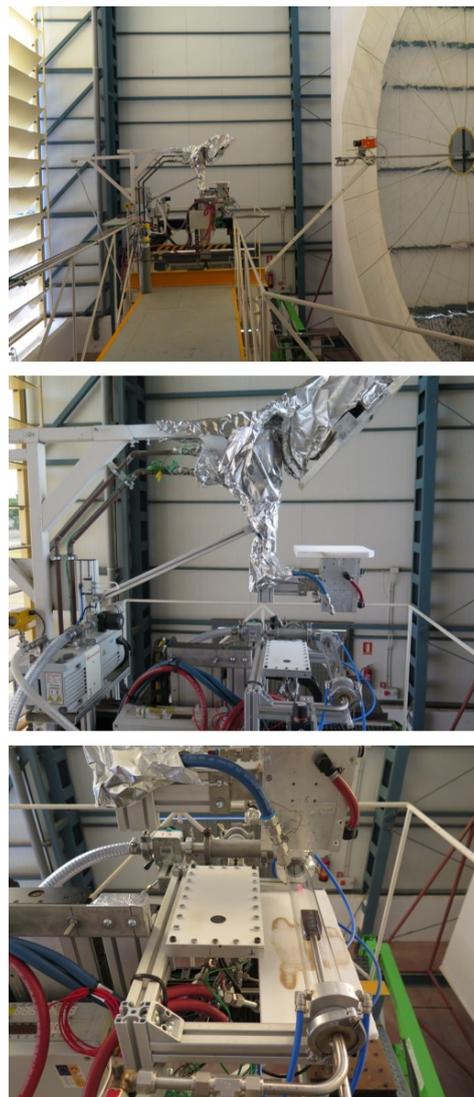
### 2.1. Sample Materials

The molybdenum (Mo) powders of nominal purity 99.9% and median particle size 2  $\mu\text{m}$  were supplied from Goodfellow (UK) and the Fe powders of nominal purity 99.9% were supplied from Alfa Aesar, now part of Thermo

Fisher Scientific Inc. (USA), defined as “sponge” product with a density of 7.86 g·cm<sup>-3</sup> and a particle size < 100 mesh (150  $\mu\text{m}$ ). Ammonia (NH<sub>3</sub>) gas used was with purity 99.8% (H<sub>2</sub>O < 0.1 ppb) and N<sub>2</sub> gas with purity 99.998% (H<sub>2</sub>O < 3 ppm; O<sub>2</sub> < 5 ppm), both supplied from Carbueros Metalicos (Air Products) S.A. (Spain).

### 2.2. Experimental Setup and Procedure

The nitriding experiments were carried out using SF40 solar furnace, with nominal power output 40 kW, at PSA (Fig. 1) whose detailed performance characteristics might be referred to elsewhere [24]. At the focal spot of the concentrated solar beam, the radiative flux reaches 7000 Suns (1 Sun = 1 kW·m<sup>-2</sup>).



**Figure 1.** Experimental setup used for nitriding Mo and Fe powders in uncracked NH<sub>3</sub> gas under heating with concentrated solar beam in SF40.

<top> Overall view with the solar beam concentrator at the right hand side, the test table at the middle and louvered shutter on the left hand side.

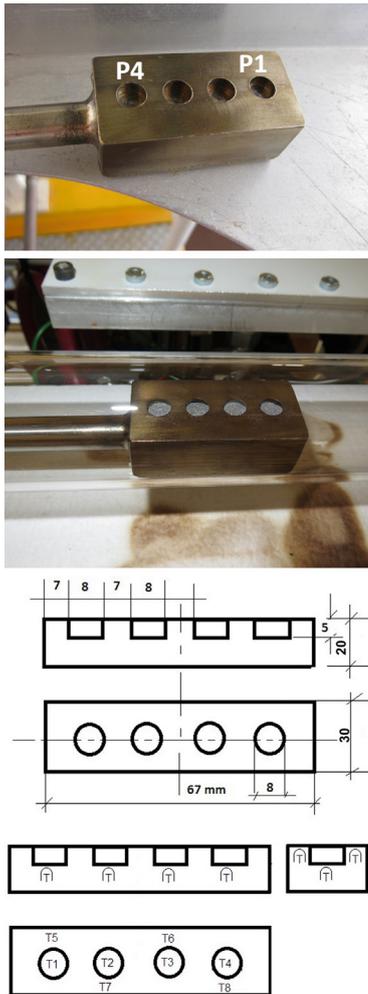
<middle> Detail of test table showing the tilted mirror (top center) together with homogenizer (below mirror) and reaction tube (bottom).

<bottom> Close-up view of the reaction tube showing sample holder below secondary concentrator

Constitution of the gas feed line was basically the same as the one integrated in the SF5 furnace [25] used for the earlier nitriding experiments in uncracked  $\text{NH}_3$  gas [7, 8, 21, 23].

The amount of sunlight incident on the concentrator (shown at right hand side edge of top picture of Fig. 1) and therefore the radiative flux was controlled by the angular motion of the louvered shutter salts (shown at left hand side edge of top picture of Fig. 1). Moreover, a tilt mirror (45°; shown at the middle of upper edge of middle picture of Fig. 1) was used to perform these tests in a horizontal plane, which turned 90° the focal beam and projected the concentrated solar beam onto the specimen holder.

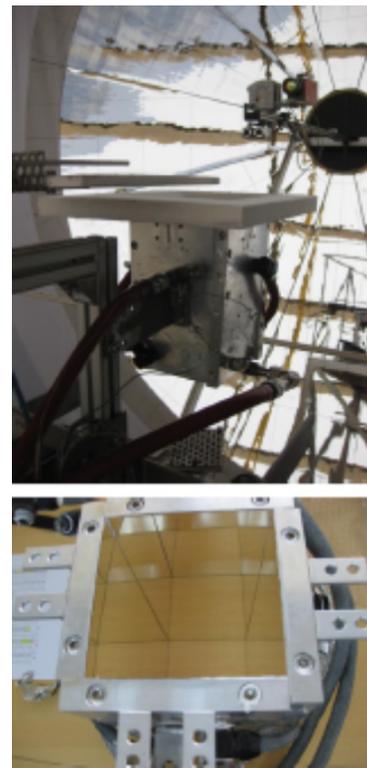
The reactor consisted of a standard 2.5 mm thick silica glass tube with inner diameter 45 mm and length about 1000 mm. Both ends of the silica tube were sealed with water-jacketed vacuum flanges to guaranty gas-tightness to avoid undesirable  $\text{NH}_3$  leaks to and  $\text{O}_2$  impurity penetration from external atmospheric environment.



**Figure 2.** Powder specimen holder made of refractory steel.  
 <top> Sample holder prior to preliminary nitriding in  $\text{NH}_3$  gas. P1 at up-stream side and P4 at down-stream side of the  $\text{NH}_3$  gas flow.  
 <middle> Appearance with the specimen powder after nitriding test run;  
 <bottom> Schematic of the holder showing its dimensions and positions of 8 thermocouples, T1 ~ T8, allocated in the specimen holder; Distance between the center of P1 and the center of P4 was 45 mm

The sample holder was specially designed and manufactured using a refractory steel. As shown in Fig. 2, four cylindrical holes (diameter 8 mm and depth 5 mm) were drilled to contain the powders of Mo or Fe to be nitrided. For exact temperature control, eight K-type thermocouples inserted through SUS316 stainless steel tube of diameter 1 cm from down-stream side of silica glass reactor tube (cf. bottom picture of Fig. 1) were set at both the top and bottom planes of the powder samples (T1 ~ T8), as illustrated schematically at the bottom of Fig. 2. For allocation of the thermocouples, 2 mm holes were drilled to about 1 mm depth from the bottom of the 4 holes for holding powder specimens (T1 ~ T4) and to about 1 mm depth from the top surface (T5 ~ T8) of the sample holder top surface. A 2 mm thick plate of the SUS316 steel was welded to the bottom of the sample holder to inhibit contact of the thermocouples with the  $\text{NH}_3$  gas.

In addition, heat flux measurements were carried out using a Gardon type radiometer ThermoGage TG1000-1, supplied from Vatel Corporation, with 0 ~ 6469  $\text{kW}\cdot\text{m}^{-2}$  range. Typically, at 900°C, radiometer reading fell around 300  $\text{kW}\cdot\text{m}^{-2}$ , whereas at 600°C, the values obtained were around 115  $\text{kW}\cdot\text{m}^{-2}$ .



**Figure 3.** Appearance of temperature homogenizer.  
 <top> General view from the side against the background solar beam concentrator.  
 <bottom> Bird's eye view looking down the interior mirror surface. Dimension of the temperature homogenizer is height 250 mm, top opening edge length 127 mm and bottom opening edge length 105 mm

Temperature homogeneity covering the entire specimen holder area was achieved by the integration of a newly developed temperature homogenizer in the path of the

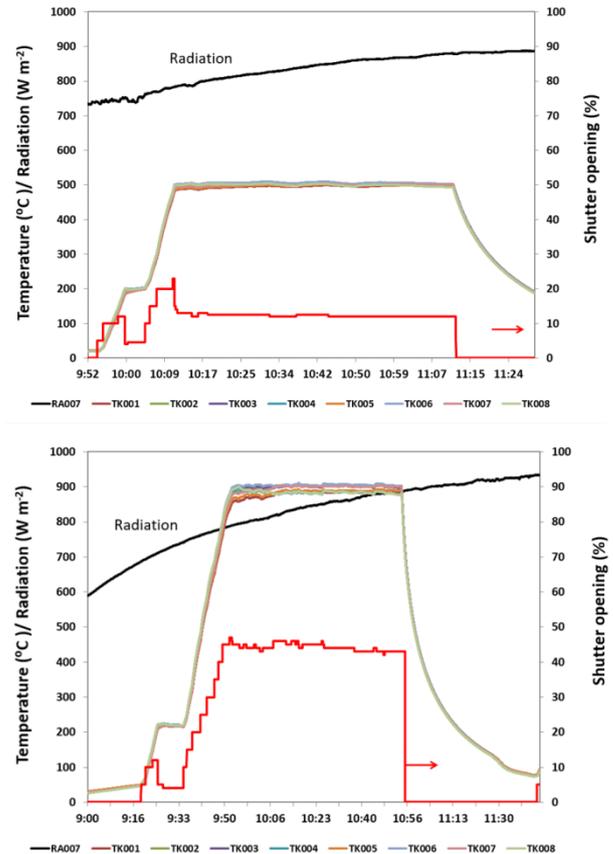
concentrated solar beam (Fig. 3). Temperature difference among the 8 K-type thermocouples fell in the range of  $\pm 5^\circ\text{C}$  (at  $500^\circ\text{C}$ ) or  $\pm 10^\circ\text{C}$  (at  $900^\circ\text{C}$ ) throughout test runs, E01 ~ E10 (Table 1) as seen in Fig. 4. This is a remarkable achievement in view of the fact that, in a previous study on temperature homogeneity in solar furnace [26], it was observed that the temperature profile around the focal spot of the concentrated beam was Gaussian yielding radial temperature difference between the focal spot centre and the focal spot periphery (e.g.,  $80^\circ\text{C}$  at  $1073\text{ K}$  measured using an AISI 310 plate receiver). Even through indirect heating using a primitive design of temperature homogenizer, results demonstrated temperature drop of around  $50^\circ\text{C}$  along the height beneath the top graphite disc (serving as receiver of concentrated solar beam) and the bottom sample holder [27]. Therefore, in order to achieve a more uniform temperature distribution throughout the test samples being exposed to the solar beam, a secondary concentrator consisting of a tronco-conical mirror kaleidoscope of square shape (around  $127\text{ mm}$  top aperture and  $105\text{ mm}$  in the bottom side, respectively) with height  $250\text{ mm}$ , hereafter called simply as temperature homogenizer, was placed over the tubular reactor (Fig. 3).

**Table 1.** List of test conditions carried out at PSA in September/October 2017 for Mo and Fe powder specimens in stream of NH<sub>3</sub> gas (uncracked NH<sub>3</sub>) under irradiation of concentration solar beam. Test runs for Fe powder specimens were shaded

Test run	Specimen	Temp. $T$ [ $^\circ\text{C}$ ]	NH <sub>3</sub> flow $v$ [ $\text{mm}\cdot\text{s}^{-1}$ ]	duration $t$ [min]
E01	Fe	500	1.14	60
E02	Fe	500	2.29	60
E03	Fe	600	1.14	60
E04	Mo	800	1.14	60
E05	Mo	900	1.14	60
E06	Mo	800	2.29	60
E07	Mo	900	2.29	30
E08	Mo	900	2.29	60
E09	Fe	600	2.29	60
E10	Mo	900	11.4	60

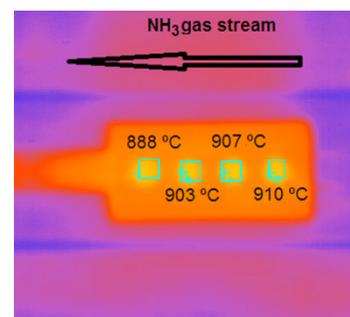
By insertion of the temperature homogenizer, not only improvement of the planar homogeneity of the temperature of the focal spot but also minimization of the time fluctuation of the arbitrary spot in the focal area was achieved as evident from the comparison between  $T$  profiles reproduced in Fig. 4 in this work with temperature homogenizer and the ones detected under similar solar irradiation experiments using SF5 solar furnace at PSA without temperature homogenizer reported earlier (Fig. 3 in [7]; Fig. 1A in [21]).

Careful readers might notice in the  $T$  vs.  $t$  profiles of Fig. 4 that, during heating period, heating was arrested for about 5 min at  $T = 200^\circ\text{C}$ . This was to ensure removal of surface oxide layer over metal powders making use of high hydriding power of uncracked NH<sub>3</sub> gas at relatively low  $T$  [13, 20, 22, 28].



**Figure 4.** Typical thermal cycles used for nitriding Fe at  $500^\circ\text{C}$  and Mo at  $900^\circ\text{C}$  under uncracked NH<sub>3</sub> gas together with shutter opening required to control temperatures in each case. In the legend, RA007 refers to solar radiation whereas TK001~TK008 refer to K-type thermocouples

High degree of homogeneity of temperature over the specimen holder along the NH<sub>3</sub> gas flow path is seen in infra-red (IR) video image reproduced in Fig. 5.



**Figure 5.** Snapshot IR video image of the sample holder together with the registered temperatures by K-thermocouples at the indicated locations

Eleven test runs were carried out during the 10-working day campaign (from 25th September to 6th October, 2017; one preliminary nitriding run for sample holder was not registered in Table 1). Nitriding of Fe powders were performed at  $500$  and  $600^\circ\text{C}$  for 60 min under flowing NH<sub>3</sub> controlled by a variable-area flow meter (VAF-M1-01M-1-0) supplied from Swagelok (USA). Similar conditions were used for nitriding Mo powders at temperatures,  $800$  and  $900^\circ\text{C}$ . Prior to the test run E01, the refractory steel sample

holder was subjected to preliminary nitriding at 500°C for 30 min in NH<sub>3</sub> gas stream at  $v = 1.14 \text{ mm}\cdot\text{s}^{-1}$  to minimize influence of fresh steel surface on extent  $\alpha$  of dissociation of NH<sub>3</sub> gas in the E01 test run and thereafter. In fact, it is well established that exposure of Fe parts to NH<sub>3</sub> results in the formation of a surface nitride layer which protects the steel material from further nitriding (e.g. [13]). After setting the powders to the refractory steel sample holder, the reactor was evacuated to 0.18 mbar by rotary vacuum pump at ambient temperature and then filled with pure nitrogen (N<sub>2</sub>) gas for flushing. This operation was repeated three times before introducing flowing ammonia (NH<sub>3</sub>) gas to the reaction chamber at ambient temperature. Powders were then heated under flow of NH<sub>3</sub> gas to a specified reaction temperature  $T$  for specified duration  $t$ . After completion of the reaction of duration  $t$  at temperature, gas was changed from NH<sub>3</sub> to N<sub>2</sub> (flowing at 5 L $\cdot$ min<sup>-1</sup> maintaining the temperature at  $T$  for 5 min). This was to ensure full substitution of the reaction chamber environment to N<sub>2</sub> gas from NH<sub>3</sub> before starting to cool down. This precaution to substitute gas from NH<sub>3</sub> to N<sub>2</sub> at the onset of cooling immediately after the end of the nitriding reaction was taken to minimize loss of N from the nitrided specimen surface during cooling.

X-ray diffraction (XRD) analysis was performed using a Panalytical XPert Pro MPD diffractometer in the Bragg-Brentano configuration. The data were collected with a step size of 0.02° using an X'Celerator 1D detector with CuK $\alpha$  radiation.

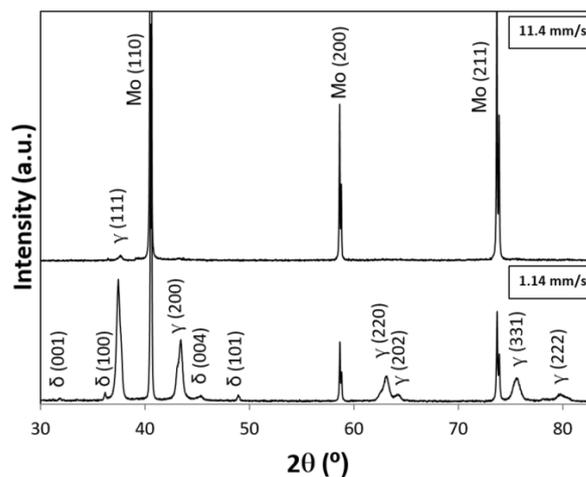
### 3. Results and Discussion

#### 3.1. Mo

XRD peak positions obtained for Mo specimens in uncracked NH<sub>3</sub> gas at different linear flow velocity  $v$  through the reaction tube at  $T = 800$  and  $900 \text{ }^\circ\text{C}$  for duration  $t = 60$  min are listed in Table 2 being compared with standard peak positions for  $\delta$ -MoN, two types of Mo<sub>2</sub>N ( $\beta$  and  $\gamma$ ) and metallic Mo. XRD patterns for Mo specimens placed at P1 position after 60 min exposure to uncracked NH<sub>3</sub> gas at  $T = 900^\circ\text{C}$  are compared in Fig. 6 between the condition with  $v = 11.4 \text{ mm}\cdot\text{s}^{-1}$  (top) and the condition with  $v = 1.14 \text{ mm}\cdot\text{s}^{-1}$  (bottom).

As seen in Table 2, at  $T = 800^\circ\text{C}$  at either  $v = 1.14$  or  $2.29 \text{ mm}\cdot\text{s}^{-1}$  at both P1 and P4 positions, reaction products were consisted of 3 phases composed of  $\delta$ -MoN,  $\gamma$ -Mo<sub>2</sub>N and metallic Mo. This result is consistent with the earlier result obtained in uncracked NH<sub>3</sub> gas with unknown  $v$  under heating with concentrated solar beam to  $T = 800^\circ\text{C}$  [7, 8]. In these two early works using concentrated solar beam as the reaction heat source, linear flow velocity  $v$  was not specified because the reaction chamber was spherical. Anyway, in conventional electric furnace (that is, under absence of light wave components),  $\delta$ -MoN became undetected when  $T$  exceeded  $725^\circ\text{C}$  (XRD pattern shown as Fig. 3 in [5]). The work reported by Yoshizawa et al. [5]

was carried out in conventional laboratory electric furnace in stream of NH<sub>3</sub> gas at  $v = 4.3 \text{ mm}\cdot\text{s}^{-1}$  for reaction duration  $t = 20$  h. Thence, it was felt quite amazing that  $\delta$ -MoN was detected in the reaction product of Mo with uncracked NH<sub>3</sub> gas at  $T = 800^\circ\text{C}$  in the preceding work carried out under solar irradiation heating although with unspecified  $v$  [7, 8]. In this work, validity of presence of  $\delta$ -MoN was confirmed at  $T = 800^\circ\text{C}$  at both  $v = 1.14$  and  $2.29 \text{ mm}\cdot\text{s}^{-1}$  under solar irradiation heating condition implying that solar irradiation was favourable for raising upper threshold temperature  $T$  for formation of  $\delta$ -MoN.



**Figure 6.** XRD patterns for Mo specimens after exposure to uncracked NH<sub>3</sub> gas at  $900 \text{ }^\circ\text{C}$  for 60 min at different NH<sub>3</sub> gas flow velocity  $v$ .

<top> at  $v = 11.4 \text{ mm}\cdot\text{s}^{-1}$  (Run E10 at P1).

<bottom> at  $v = 1.14 \text{ mm}\cdot\text{s}^{-1}$  (Run E04 at P1).

Note that, at  $v = 11.4 \text{ mm}\cdot\text{s}^{-1}$ , nitriding to  $\delta$ -MoN failed to proceed while, at  $v = 1.14 \text{ mm}\cdot\text{s}^{-1}$  at both P1 and P4 positions, XRD peaks identifiable as  $\delta$ -MoN were detectable, although very weak, besides those identifiable as  $\gamma$ -Mo<sub>2</sub>N and metallic Mo

As such, although the mechanism of pushing up the upper threshold  $T$  for  $\delta$ -MoN formation remains unknown, experimental evidence points out clearly that presence of concentrated solar beam wave components besides infra-red (IR) heating effect contributed somehow towards synthesis of higher nitride  $\delta$ -MoN.

When  $v$  was increased to  $11.4 \text{ mm}\cdot\text{s}^{-1}$  at  $T = 900 \text{ }^\circ\text{C}$  with the intention of raising  $a(\text{N})$  by suppression of dissociation of NH<sub>3</sub> gas to promote formation of  $\delta$ -MoN, effect was adversary to cease yield of  $\delta$ -MoN in the reaction product (Table 2 and Fig. 6). This was somewhat surprising in view of  $v$ -dependence of  $a(\text{N})$  but might be understood rationally in view of stability of adsorption of NH<sub>3</sub> molecules onto Mo particles surface. For nitriding reaction of Mo to be initiated by adsorbed NH<sub>3</sub> molecules, NH<sub>3</sub> molecules must reside sufficiently long duration over Mo surface. It is suspected that, at  $v = 11.4 \text{ mm}\cdot\text{s}^{-1}$ , the residence time of NH<sub>3</sub> molecules onto Mo surface was cut short and penetration of N atoms to Mo matrix failed to take place. Thus, certain upper threshold  $v$  for realization of nitriding reaction must be defined. Judging from the results of this work, it must be no faster than  $10 \text{ mm}\cdot\text{s}^{-1}$ .



- [a] The peak position identifiable as  $\delta$ -MoN is indicated with **bold** letters.
- [b] The reference values of  $2\theta_{Cu}$  for MoN and for Mo<sub>2</sub>N were converted from the reported values by G. Hägg (Z. Phys. Chem., **B7** (1930) 339-362; Röntgenuntersuchungen über molybdän- und wolframnitride) noting that  $\theta$  defined by Hägg (1930) corresponds to  $2\theta$  in the current conventional definition of the XRD angle.
- [c] The reference values of  $2\theta_{Cu}$  for metallic Mo (shaded) were taken from the table in a monograph authored by E.K. Storms (The Refractory Carbides, Academic Press, New York, 1967).
- [d] The (*hkl*) index values given in parentheses in the table were not identified by the original work by Hägg (1930) but were designated later in ICDD card (No. 00-025-1367 for  $\delta$ -MoN and No. 00-004-0787 for Al sample holder). The  $2\theta_{Cu}$  (*hkl*) values in the ICDD card were not exactly in agreement with the corresponding counterparts reported by Hägg (1930).
- [e] P1  $\rightarrow$  P4: on going from up-stream side to down-stream side of NH<sub>3</sub> gas flow.

**Table 3.** XRD (X-ray diffraction) peak positions (CuK $\alpha$ ) detected for Fe specimens exposed to stream of NH<sub>3</sub> gas flow under irradiation of concentrated solar beam for 60 min with identification of phases being compared with reference peak positions for  $\alpha$ -Fe,  $\gamma$ -Fe<sub>4</sub>N and  $\epsilon$ -Fe<sub>2</sub>N phases

$2\theta_{hkl}$ (degree)	<i>h k l</i>	observed $2\theta_{Cu}$ (degree)																						
		500 °C / 60 min						600 °C / 60 min																
		1.14 mm s <sup>-1</sup>		2.29 mm s <sup>-1</sup>		1.14 mm s <sup>-1</sup>		2.29 mm s <sup>-1</sup>		1.14 mm s <sup>-1</sup>		2.29 mm s <sup>-1</sup>												
	$\alpha$ -Fe																							
	$\gamma$ -Fe <sub>4</sub> N																							
	$\epsilon$ -Fe <sub>2</sub> N																							
23.47	1 0 0																							
33.43	1 1 0																							
38.32				1 0 0	37.84	37.89	37.90	38.21	38.22	38.23	38.20													
41.23				0 0 2	41.16	41.17	41.17	41.19	41.20	41.17	41.16													
<b>41.26</b>	<b>1 1 1</b>																							
<b>43.73</b>				<b>1 0 1</b>	<b>43.24</b>	<b>43.30</b>	<b>43.25</b>	<b>43.61</b>	<b>43.62</b>	<b>43.64</b>	<b>43.61</b>													
<b>44.71</b>	<b>1 0 0</b>				44.74	44.71	44.74																	
48.01					47.90	47.90	47.89																	
54.11																								
57.54				1 0 2	56.97	56.95	56.96	57.39	57.40	57.39	57.39													
59.77				2 1 1																				
	<b>Phases identified</b>				$\epsilon$ -Fe <sub>2</sub> N $\gamma$ -Fe <sub>4</sub> N $\alpha$ -Fe	$\epsilon$ -Fe <sub>2</sub> N $\gamma$ -Fe <sub>4</sub> N $\alpha$ -Fe	$\epsilon$ -Fe <sub>2</sub> N $\gamma$ -Fe <sub>4</sub> N $\alpha$ -Fe	$\epsilon$ -Fe <sub>2</sub> N $\gamma$ -Fe <sub>4</sub> N $\alpha$ -Fe	$\epsilon$ -Fe <sub>2</sub> N															

[a] The most intense diffraction line index (*hkl*) for each reference compound and the most intense observed  $2\theta_{Cu}$  for each specimen are indicated with **bold** letters. As seen in the above table, the most intense XRD peaks of any examined phase fell in the range of  $2\theta_{Cu}$  between 41° and 45°.

[b] The reference values of  $2\theta_{Cu}$  for Fe compounds are reproduced from a monograph compiled by Liedtke (Nitrieren und Nitrocarburieren, Wärmebehandlung von Eisenwerkstoffen II, 5th Edition, Expert-Verlag GmbH, Remmingen, 2010).

[c] P1  $\rightarrow$  P4: on going from up-stream side to down-stream side of NH<sub>3</sub> gas flow.

In the nitriding experiment using uncracked NH<sub>3</sub> gas at  $v = 4.3 \text{ mm}\cdot\text{s}^{-1}$  (corresponding to volumetric flow rate  $200 \text{ mL}\cdot\text{min}^{-1}$ ), nitriding process for Mo proceed all right in a conventional electric furnace with silica reaction tube [5].

Thus, the upper threshold level of  $v$  for realization of nitriding in NH<sub>3</sub> gas stream must be somewhere between 5 and  $10 \text{ mm}\cdot\text{s}^{-1}$ .

Looking at results for Mo specimen nitrided using NH<sub>3</sub> stream at  $v = 2.29 \text{ mm}\cdot\text{s}^{-1}$  at  $900^\circ\text{C}$  (Table 2), small XRD peak referring to  $\delta$ -MoN (100) remained detectable at P1 position (up-stream side) but, at P4 position (down-stream side), no XRD peak identifiable as  $\delta$ -MoN was detectable. Thus, at  $v = 2.29 \text{ mm}\cdot\text{s}^{-1}$  at  $900^\circ\text{C}$ , nitriding power of uncracked NH<sub>3</sub> gas became insufficient to yield  $\delta$ -MoN in the down-stream side provided that surface coverage rate of Mo powders with uncracked NH<sub>3</sub> gas was determined as a function of  $v$  along the gas flow path.

Thus, judging from the results summarized in Table 2, optimum  $T$  for nitriding with uncracked NH<sub>3</sub> gas must be  $800^\circ\text{C}$  which is by about  $100^\circ\text{C}$  higher than the upper threshold  $T$  for  $\delta$ -MoN synthesis in conventional electric furnace under absence of light wave components.

Accordingly, use of concentrated solar beam as the reaction heat source for higher nitride formation for Mo in uncracked NH<sub>3</sub> gas environment was concluded beneficial in view of acceleration of the reaction rate through increasing  $T$  without causing dissociation of  $\delta$ -MoN like in the experiment in a conventional laboratory electric furnace at  $T \geq 725^\circ\text{C}$  [4,5].

In this experiment, lower threshold  $v$  was not determined due to limitation of minimum NH<sub>3</sub> gas flow rate reading of the used variable-area flow meter. It is guessed that the lower threshold  $v$  for higher nitride formation for Mo might fall in a range between  $0.1$  and  $1 \text{ mm}\cdot\text{s}^{-1}$ . In view of realization of nitriding with minimized resource consumption (in this case, amount of NH<sub>3</sub> gas spent for the nitriding reaction), determination of lower threshold  $v$  is of pragmatic industrial importance than determination of higher threshold  $v$ .

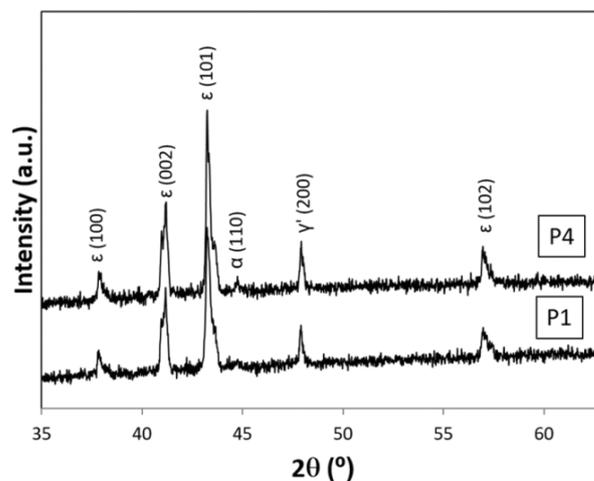
Anyway, it must be kept in mind that such threshold  $v$  values determined experimentally is valid only to a specific experimental setup and not as universally acceptable experimental parameter values. For example, the present experimental setup was made with transparent silicate glass tube furnace with steel specimen holder while that used by Yoshizawa *et al.* [5] was made with quartz tube furnace with alumina specimen holder. Depending on these reactor components, extent of dissociation of NH<sub>3</sub> gas might be affected.

### 3.2. Fe

Literature information [7, 10-15] demonstrated that synthesis of  $\epsilon$ -Fe<sub>2</sub>N through reaction at normal pressure can be realized only by use of uncracked NH<sub>3</sub> but not in N<sub>2</sub> gas environment.

According to XRD results for Fe specimen summarized in

Table 3, optimum reaction  $T$  for synthesis of  $\epsilon$ -Fe<sub>2</sub>N in uncracked NH<sub>3</sub> gas must be  $600^\circ\text{C}$  under irradiation with concentrated solar beam in the present experimental setup. In the preceding report [7], reaction product from Fe pellet specimen was consisted of  $\epsilon$ -Fe<sub>2</sub>N co-existed with  $\gamma'$ -Fe<sub>4</sub>N by nitriding in uncracked NH<sub>3</sub> gas at  $600^\circ\text{C}$  under solar irradiation heating in spherical quartz glass reactor. This would mean that  $a(\text{N})$  of uncracked NH<sub>3</sub> gas at the spot of Fe pellet must have been dropped to a level insufficient to yield single-phase  $\epsilon$ -Fe<sub>2</sub>N in the earlier work [7]. In the preceding experiment [7], 11 compacted disc specimens were exposed to uncracked NH<sub>3</sub> gas in a spherical Pyrex glass reactor chamber in which flow pattern of NH<sub>3</sub> gas was unknown. Disc specimens were used in that work to carry out maximum number of nitriding experiments in uncracked NH<sub>3</sub> gas without risking cross contamination among specimens of unlike metals. Increased number of specimens might have resulted in promoted dissociation of NH<sub>3</sub> to lead to drop of  $p(\text{NH}_3)$  and resultant decrease of  $a(\text{N})$  to a level insufficient to yield single-phase  $\epsilon$ -Fe<sub>2</sub>N.



**Figure 7.** XRD patterns for Fe specimens after exposure to uncracked NH<sub>3</sub> gas at  $500^\circ\text{C}$  for 60 min at NH<sub>3</sub> gas flow velocity  $v = 1.14 \text{ mm}\cdot\text{s}^{-1}$  (Run E01) at P1 (bottom) and at P4 (top). Note that, at down-stream side (P4), weak XRD peak identifiable as  $\alpha$ -Fe (110) was detectable while this peak was not detectable at up-stream side (P1)

It is intriguing to note in Table 3 and in Fig. 7 that, under nitriding with uncracked NH<sub>3</sub> gas at  $v = 1.14 \text{ mm}\cdot\text{s}^{-1}$  at  $500^\circ\text{C}$  under irradiation of concentrated solar beam, remnant of metallic  $\alpha$ -Fe was detected at P4 (down-stream side) but not at P1 (up-stream side) implying gradual decrease of  $a(\text{N})$  of uncracked NH<sub>3</sub> along the NH<sub>3</sub> gas flow path. This trend was clearly demonstrated experimentally by Nishimaki *et al.* [14] for hypo-stoichiometric  $\epsilon$ -Fe<sub>2</sub>N. At  $v = 2.29 \text{ mm}\cdot\text{s}^{-1}$  in which  $a(\text{N})$  at the corresponding spot along the NH<sub>3</sub> gas flow path was anticipated to be higher than that at  $v = 1.14 \text{ mm}\cdot\text{s}^{-1}$ , remnant of  $\alpha$ -Fe was detected at P1 as well as at P4. This seemed a bit queer with reference to  $a(\text{N})$  alone but, as pointed out earlier in the text referring to Table 2 and Fig. 6 for the nitriding reaction for Mo specimen, the first step of nitriding process is the adsorption of NH<sub>3</sub> gas molecules onto

the metal surface. The faster the NH<sub>3</sub> gas flow rate, the higher the likelihood of removal of once adsorbed NH<sub>3</sub> gas molecules from the metal surface. Thus, it was speculated that rate of coverage of Fe surface by adsorbed NH<sub>3</sub> molecules might become lower with  $v = 2.29 \text{ mm}\cdot\text{s}^{-1}$  than with  $v = 1.14 \text{ mm}\cdot\text{s}^{-1}$ .

Thus, on undertaking experiment using inherently unstable uncracked NH<sub>3</sub> gas molecules as a nitriding medium, it must be remembered that nitriding efficiency is dependent on density of surface coverage with adsorbed NH<sub>3</sub> molecules (this would tend to decrease with increasing  $v$ ) as well as on  $a(\text{N})$  (this tends to increase with increasing  $v$ ) and thence the optimum  $v$  might be determined for specific configuration of the experimental setup. For example, when adequate catalytic substance is discovered for promoting re-combination of N<sub>2</sub> and H<sub>2</sub> to yield NH<sub>3</sub>, high  $a(\text{N})$  of uncracked NH<sub>3</sub> gas might be held at a level satisfactorily high to yield higher nitride phase in the reaction product even at slow  $v$ .

### 3.3. Merits and Limitations of Using Uncracked NH<sub>3</sub> Gas as a Nitriding Agent

In this work, merits of using uncracked NH<sub>3</sub> gas as a nitriding medium for metals, that are difficult to be converted to higher nitride,  $\delta\text{-MoN}$  and  $\epsilon\text{-Fe}_2\text{N}$ , through reaction with N<sub>2</sub> gas, were demonstrated under condition of heating with concentrated solar irradiation (see also [7, 8]). Compared with VIa-group metals (Cr, Mo and W), IVA-group metals (Ti, Zr and Hf) and Va-group metals (V, Nb and Ta) are relatively easily nitrated to yield mono-nitride MN straight away from M in N<sub>2</sub> gas under normal pressure at  $T$  higher than 1200°C and thence it is not a common habit to use uncracked NH<sub>3</sub> gas as a nitriding medium for IVA- and Va-group metals. However, in recent works using solar furnace as a source of reaction heat, low temperature nitriding of IVA- and Va-group metals in uncracked NH<sub>3</sub> gas was attempted [21, 23]. These works were done noting the empirical knowledge that presence of partially nitrated metal MN <sub>$x$</sub>  ( $x < 1$ ) being mixed with M in the starting material is favourable for minimizing dimensional distortion of final consolidated nitride ceramic component on production from compacted powder by self-propagating combustion synthesis (cf. for example, Gromov and Chukhlomina [9]). Results of the work of low temperature nitriding of IVA- and Va-group metals in uncracked NH<sub>3</sub> gas under solar irradiation heating showed that, in spite of relatively low reaction temperature ( $< 1000^\circ\text{C}$ ), evidence of progress of partial nitriding was detected [21, 23]. Such partially nitrated powders might be accepted as a starting material for near-net shape production process by self-propagating combustion synthesis.

In the following, merits and problematic aspects of nitriding using uncracked NH<sub>3</sub> gas as a nitriding agent are reviewed.

Uncracked NH<sub>3</sub> gas is inherently an unstable substance and accordingly its extent  $\alpha$  of dissociation (cf. Eq. (1)) is determined basically as functions of temperature  $T$  and linear

flow velocity  $v$  of NH<sub>3</sub> gas. However, even in a given experimental setup,  $\alpha$  would not hold constant along the NH<sub>3</sub> gas flow path showing steady rise of  $\alpha$  along the flow path and resultant steady decrease of  $a(\text{N})$  of uncracked NH<sub>3</sub> gas on going from up-stream side to down-stream side. This characteristic of flowing NH<sub>3</sub> gas was experimentally demonstrated by Nishimaki et al. [14] as steady decrease of N content in synthesized hypo-stoichiometric  $\epsilon\text{-Fe}_2\text{N}$  evidenced by lattice parameter change along the NH<sub>3</sub> gas flow path determined by XRD analysis (Fig. 3 in [14]).

Accepting isothermal expression for  $a(\text{N})$  of uncracked NH<sub>3</sub> gas drawn by Katsura [28] on the basis of thermodynamic consideration given as functions of  $p(\text{NH}_3)$ ,  $p(\text{H}_2)$  and  $K_p$ , the expression for  $a(\text{N})$  is eventually represented as functions of extent  $\alpha$  of dissociation of NH<sub>3</sub> gas and  $K_p$  at arbitrary  $T$

$$\begin{aligned} a(\text{N}) &= (1/K_p) \cdot \{p(\text{NH}_3)/p(\text{H}_2)^{3/2}\} = (1/K_p) \cdot [(1-\alpha)/(3\alpha/2)^{3/2}] \\ &= (1/K_p) \cdot (2/3)^{3/2} \cdot (1-\alpha)/\alpha^{3/2} \end{aligned} \quad (2)$$

where  $K_p$  refers to equilibrium constant for formation of 1 mole of NH<sub>3</sub> gas from 1/2 mole of N<sub>2</sub> gas and 3/2 mole of H<sub>2</sub> gas.

On the other hand, isothermal expression for  $a(\text{H})$  of uncracked NH<sub>3</sub> gas at arbitrary  $T$  as functions of  $\alpha$  and  $K_p$  is drawn likewise

$$\begin{aligned} a(\text{H}) &= \{(1/K_p) \cdot [p(\text{NH}_3)/p(\text{N}_2)^{1/2}]^{1/3}\} \\ &= (2/K_p^2)^{1/6} (1-\alpha)^{1/3} / \alpha^{1/6} \end{aligned} \quad (3)$$

Isothermal  $a(\text{N})$  vs.  $\alpha$  relationships and isothermal  $a(\text{H})$  vs.  $\alpha$  relationships are exhibited graphically in [20, 22, 28-31] demonstrating very high extent of  $a(\text{N})$  enhancement and modest extent of  $a(\text{H})$  enhancement through retardation of dissociation of NH<sub>3</sub> gas.

Indirect evidence of high power of hydriding of uncracked NH<sub>3</sub> gas was demonstrated experimentally by Shohoji et al. [13] on surface nitriding of steel ingot block specimen in which surface nitriding layer of homogeneous thickness was detected for the test pieces heated in NH<sub>3</sub> gas flow from the beginning of heating from ambient temperature till the end of  $t$  hour reaction at 500°C and then cooled down in N<sub>2</sub> gas flow (AN- $t$  specimens in the designation in [13] whereas surface nitriding failed to proceed for the steel ingot specimen heated in flow of N<sub>2</sub> gas from ambient temperature to the reaction temperature and NH<sub>3</sub> was introduced only when the reaction temperature 500°C was reached (NA- $t$  specimens). This difference between AN- $t$  and NN- $t$  specimens appeared to indicate that surface oxide layer was not removed from the steel block specimen during heating in N<sub>2</sub> gas environment (NA- $t$  specimen) whereas surface oxide layer was removed during heating in NH<sub>3</sub> gas (AN- $t$  specimen) to allow nitridation at the reaction temperature 500°C.

On the other hand, the steel ingot specimen heated from ambient temperature to 500°C in NH<sub>3</sub> gas stream, held at this reaction temperature for  $t$  hours and cooled down in NH<sub>3</sub> stream (AA- $t$  specimens) showed certain extent of N loss from the surface compared with that in the AN- $t$  specimen at the comparable  $t$  suggesting that N removal from the

specimen surface took place during cooling in NH<sub>3</sub> gas stream down to ambient temperature. Thickness of surface nitrated layer in the AA-*t* specimen became irregular while that in the AN-*t* specimen was homogeneous (cf. Table 2 and Fig. 3 in [13]).

As such, uncracked NH<sub>3</sub> gas at relatively low temperature (probably < 300°C) would act as a hydriding agent rather than a nitriding agent. Therefore, on undertaking nitriding of metal in uncracked NH<sub>3</sub> gas, it is of essential importance to start NH<sub>3</sub> gas flow from the beginning of heating from ambient temperature to ensure removal of surface oxide layer from the specimen to be nitrated during the heating process to the reaction temperature. On the other hand, when the reaction in uncracked NH<sub>3</sub> gas at specified temperature is finished, nitrated specimen must be cooled down in N<sub>2</sub> gas as fast as possible. When NH<sub>3</sub> gas is continued to be flown during the period of cooling down to ambient temperature, undesired loss of N from the nitrated specimen would proceed on account of high hydriding power of uncracked NH<sub>3</sub> gas at relatively low *T*.

Likewise, it was demonstrated by Katsura and co-workers [17-19] that N-enriched hyper-stoichiometric sesqui-nitride  $\alpha$ -U<sub>2</sub>N<sub>3+x</sub> of uranium (U) possessing *x* value that could not be formed in N<sub>2</sub> gas environment was synthesized in uncracked NH<sub>3</sub> gas environment at normal pressure.

On nitriding of metal powders using uncracked NH<sub>3</sub> gas as a nitriding medium, excessive refinement of powder particles size does not seem to be favourable. Indeed, Nishimaki *et al.* [15] reported that, at comparable flow rate ~20 mL·min<sup>-1</sup> at *T* = 550°C,  $\epsilon$ -Fe<sub>2</sub>N was synthesized from coarse Fe particles with mean diameter 150  $\mu$ m (estimated  $\alpha$  = 0.01 to yield  $a(N) = 4 \times 10^4$ ) but  $\gamma'$ -Fe<sub>4</sub>N formed from fine 10 nm Fe particles (estimated  $\alpha$  = 0.30 to yield  $a(N) = 3.6 \times 10^2$ ). Drop of  $a(N)$  by 2 orders of magnitude with fine 10 nm Fe particles from that with coarse 150  $\mu$ m Fe (Table 1 in [15]) was interpreted to be caused by extensiveness of effective surface area of 10 nm Fe particles compared with that of 150  $\mu$ m Fe particles. As such, even starting material's surface condition might modify  $\alpha$  and resultantly  $a(N)$  of uncracked NH<sub>3</sub> gas. In fact, in the preceding work of nitriding of Fe particles at 550°C in uncracked NH<sub>3</sub> gas under concentrated solar irradiation heating [7], some results were a bit puzzling; after reaction duration *t* = 30 min, the reaction product was single-phase  $\epsilon$ -Fe<sub>2</sub>N but, when *t* was prolonged to 90 min, the reaction product was reduced down to single phase  $\gamma'$ -Fe<sub>4</sub>N (Table 3 in [7]). This might be interpreted as follows;  $a(N)$  in uncracked NH<sub>3</sub> gas at early stage of the reaction (*t* ≤ 30 min) was high enough to convert Fe powders to single-phase  $\epsilon$ -Fe<sub>2</sub>N but the formed  $\epsilon$ -Fe<sub>2</sub>N promoted dissociation of NH<sub>3</sub> gas to lead to decrease of  $a(N)$  of the uncracked NH<sub>3</sub> gas to turn the reaction product to single-phase  $\gamma'$ -Fe<sub>4</sub>N at *t* = 90 min. This aspect requires further experimental verification to validate reproducibility. Anyway, such somewhat queer *t*-dependence of reaction product constitution formed in uncracked NH<sub>3</sub> gas environment appeared to warn of interactive nature of

uncracked NH<sub>3</sub> gas with reaction product itself as well as with reactor tube surface and sample holder.

Keeping this aspect in mind, preliminary nitriding of the refractory steel sample holder was done in NH<sub>3</sub> gas stream without the sample powders prior to E01 test run (Table 1) as a precaution to avoid uncontrolled influence of NH<sub>3</sub> dissociation mode affected by nitriding process of sample holder on the target reaction of Fe nitriding in the E01 test run. Sample holder with bronze surface colour shown in the picture second from the top in Fig. 2 was the one after being subjected to preliminary surface nitriding in NH<sub>3</sub> flow 1.14 mm·s<sup>-1</sup> at 500 °C for 30 min. The surface colour of the initial state of the refractory steel sample holder was whitish silver.

Noting these realities with regard to use of inherently unstable uncracked NH<sub>3</sub> gas as a nitriding medium, it must be kept in mind that  $\alpha$  and thence  $a(N)$  cannot be considered as a universal experimental parameter dependent largely on *T* and *v* alone for different experimental setup and sample material. The lower and upper *v* levels set for a given *T* and for a specified sample material in a given reactor system are quite likely to change in another reactor setup.

On nitriding process using uncracked NH<sub>3</sub> gas as a nitriding medium, there is no risk of introduction of impurity H atoms into the synthesized metal nitride. Temperature window for stability of metal hydride lays is incomparably lower range than that for stability of metal nitride. Anyway, on account of modestly enhanced  $a(H)$  of uncracked NH<sub>3</sub> gas molecules at relatively low *T* (< 300°C), reduction of surface scale layer existing over the metal powders used as the starting material would proceed during heating in NH<sub>3</sub> gas flow [13, 28, 31]. To ensure reduction removal of surface oxide layer by action of H in uncracked NH<sub>3</sub> gas, deliberate *T* arrest at 200°C for about 5 min was arranged during heating (cf. Fig. 4).

It is also speculated that, for nitriding of metal using uncracked NH<sub>3</sub> gas, modest grade of NH<sub>3</sub> gas containing certain H<sub>2</sub>O impurity might be used as a nitriding medium because undesired oxidation reaction by impurity H<sub>2</sub>O might be preceded by reduction reaction by H with high  $a(H)$  in the uncracked NH<sub>3</sub> gas [28, 31]. This aspect must be considered as one of pragmatic merits of using uncracked NH<sub>3</sub> gas as a nitriding medium in industrial metal nitride production.

## 4. Conclusions

Linear reaction tube made of silica glass and sample holder made of refractory steel were newly designed and composed to carry out nitriding experiments for powder specimens of Mo and Fe in uncracked NH<sub>3</sub> gas at specified linear flow rate *v* under irradiation of concentrated solar beam in SF40 solar furnace at PSA and following conclusions were drawn.

(1) Higher nitrides of Mo ( $\delta$ -MoN) and Fe ( $\epsilon$ -Fe<sub>2</sub>N) were successfully synthesized using the newly developed experimental setup in stream of NH<sub>3</sub> gas with controlled flow rate under irradiation of concentrated solar beam.

(2) At a fixed spot of reactor tube, chemical activity  $a(N)$  of uncracked  $NH_3$  gas varied as functions of  $NH_3$  gas flow velocity  $v$  and temperature  $T$  and constitution of the synthesized nitride phases varied accordingly.

(3) At specified  $v$  and  $T$ ,  $a(N)$  tended to decrease on going from up-stream side to down-stream side on account of inevitable progress of dissociation of  $NH_3$  gas along the gas flow path to weaken nitriding power of uncracked  $NH_3$  gas on going from up-stream side to down-stream side.

(4) Generally, increasing flow velocity  $v$  was found to be beneficial to raise nitriding power of uncracked  $NH_3$  gas but, when  $v$  exceeded certain threshold value, nitriding power of uncracked  $NH_3$  was not gained due to insufficiency of contact between  $NH_3$  gas and metal surface.

(5) Optimized nitriding condition using uncracked  $NH_3$  gas must be determined for specified experimental setup because extent  $\alpha$  of dissociation of  $NH_3$  gas must be affected by reaction components materials and their surface conditions as well as by the reactant material.

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