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Low-temperature short-time nitriding of Va-group metals, V, Nb and Ta, in uncracked NH₃ gas under heating with concentrated solar power (CSP)

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Abstract

Over the last two decades, the authors have been using concentrated solar beam as the reaction heat source for synthesizing carbides and nitrides of *d*-group transition elements in view of usage of ecological renewable energy source in place of conventional heat sources using electricity or natural gas. In recent works, nitriding of VIa-group metals (Cr, Mo, W) and Fe in stream of NH₃ gas with suppressed extent of dissociation (uncracked NH₃) was attempted under heating with concentrated solar beam. It was demonstrated that mono-nitride δ -MoN of Mo and sub-nitride ϵ -Fe₂N of Fe that are known to be impossible to synthesize in N₂ gas environment even at elevated N₂ gas partial pressure $p(\text{N}_2)$ up to 300 bar were successfully synthesized by the reactions of these metals in stream of NH₃ gas under heating with concentrated solar beam up to 800°C.

In the present work, nitriding of Va-group metals (V, Nb and Ta) was attempted in stream of NH₃ gas under irradiation of concentrated solar beam. After 90 min heating in uncracked NH₃ under concentrated solar beam up to 800°C, X-ray diffraction (XRD) characterization of the reaction products showed certain extent of nitriding progressed for all the specimens in spite of relatively low reaction temperature for short reaction duration.

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1. Introduction

Carbides and nitrides of *d*-group transition metals (Ti, Zr, Hf, V, Nb, Ta; Cr, Mo, W) are classified as refractory hard metals and they are with significant industrial importance [1-5]. In recent years, these compounds are also considered as functional materials (e.g., δ -MoN as superconductor [6] and carbides and nitrides as hydrogen-evolving electro-catalyst [7]).

Synthesis of these carbides and nitrides carried out at high temperature (typically > 1700 K) is highly energy-consuming process and thence, in view of saving conventional energy in form of electricity or gas, the authors have attempted a series of experiments to synthesize carbides using concentrated solar beam as the ecological renewable reaction heat source at PSA (Plataforma Solar de Almería, Tabernas, Spain) and at PROMES-CNRS (Laboratoire Procédés, Matériaux et Energie Solaire, Odeillo, France). The acquired results demonstrated that concentrated solar beam is a suitable heat source for synthesizing both refractory carbides and nitrides. Indeed, evidence gathered suggests that these compounds were with satisfactory quality to be

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accepted as raw powder materials for further processing to manufacture non-oxide ceramic components.

In a series of experiments carried out in September 2012 at PSA using vertical type solar furnace SF5 [8], we attempted synthesizing higher nitrides of Mo (δ -MoN) and Fe (ϵ -Fe₂N) in stream of NH₃ gas with suppressed extent of dissociation (uncracked ammonia gas) that are not synthesized in N₂ gas atmosphere even at very high partial pressure $p(\text{N}_2)$ and the results were published elsewhere [9,10]. Successful synthesis of δ -MoN was first reported by Hägg in 1930 [11] and, in the same year, Lehrer [12] reported synthesis of ϵ -Fe₂N phase in uncracked NH₃ gas. Extremely high chemical potential $a(\text{N})$ of N in uncracked NH₃ and modestly high chemical potential $a(\text{H})$ of H in uncracked NH₃ were appreciated rationally in terms of thermodynamics by Katsura in 1992 [13].

By nitriding Mo in stream of NH₃ gas in conventional electric furnace, δ -MoN was synthesized at 700°C but it dissociated into γ -Mo₂N by mere rise of temperature to 725°C [14]. However, under heating with concentrated solar beam in stream of NH₃ gas, temperature range of formation for δ -MoN was extended up to 800°C [9,10]. Reason for this extension of temperature range for formation of δ -MoN in uncracked NH₃ under heating with solar beam remains unclear but it might possibly be interpreted in terms of contribution of some visible light wave components contained in the solar beam.

Synthesis of mono-nitride of Va-group metals (V, Nb and Ta) is not especially difficult in N₂ gas environment and thence there is no absolute necessity of using uncracked NH₃ gas as a nitriding medium for Va-group transition metals. But, for curiosity, the authors attempted to use flowing NH₃ gas as a nitriding medium for IVa- and Va-group metals under heating with concentrated solar beam up to temperature 800°C. Data compiled for IVa-group metals, Ti and Zr, were published elsewhere [15]. As demonstrated by XRD analysis, reaction products were consisted of mono-nitride MN co-existent with sub-nitride M₂N in spite of relatively low reaction temperature used (due to demand for maintaining extent of dissociation of flowing NH₃ gas at satisfactorily low level, it is not preferable to use temperature exceeding 1000°C). Such reaction product consisting of MN and M₂N might be of no straightforward industrial application but it might be accepted as precursor for MN synthesis by subsequent conventional industrial nitriding process with reduced reaction time.

2. Experimental

Disc samples of diameter 8 mm and height about 5 mm were uniaxially compacted at a pressure 400 MPa from metal powders of V, Nb and Ta to be subjected to nitridation reactions in the vertical axis solar furnace SF5 at PSA in flowing NH₃ gas [8]. Details of the experimental procedures might be referred to elsewhere [9,10].

Specifications of the reagents used in the present work are listed in Table 1.

Table 1. Specifications of reagents used.

Reagent	Purity (%)	Particle size (μm)	Supplier
V	99	< 45	Goodfellow(Cambridge,UK)
Nb	99.5	< 125	L.Light (Cambridge, UK)
Ta	99.9	< 75	Goodfellow(Cambridge,UK)
NH ₃	99.8	–	Carbueros Metalicos, Spain
N ₂	99.998	–	Carbueros Metalicos, Spain

Samples were placed on a 3.25 mm thick zirconia felt holder (type ZYF-A2.13 supplied by Zircar Zirconia Inc, Florida, USA) concentrically so that each of disc was placed at a distance 15 mm from the centre of circular sample holder and they were set in a 5 L spherical reaction chamber made of Pyrex glass (Fig. 2). A K-type thermocouple (K-TC) was placed at the position with distance from the holder center being equal to the center of the disc specimen (see Fig. 2).

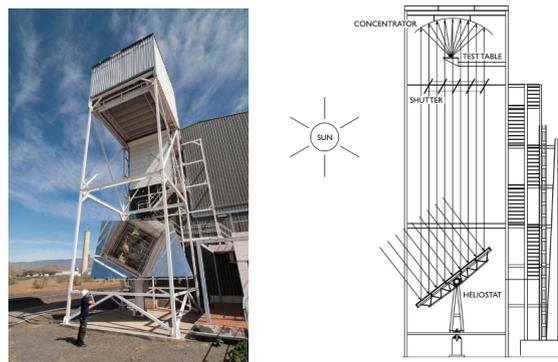


Fig. 1. Vertical axis solar furnace SF5 at PSA (reproduced from Fig. 1 in Rodríguez et al. [8]).

The chamber was then evacuated using a rotary pump and flushed with pure N₂ gas to remove away O₂ impurities. This procedure was repeated twice prior to introduction of NH₃ gas at a flow rate 10 L/h at

ambient temperature. Thereafter, by opening louvered shutter with controlled rate, specimens were heated by irradiating concentrated solar beam at top surface of the pellets to raise the temperature to a target level to hold the temperature at the specified level for 30 or 90 min. Typically, it took less than 5 min to reach the target temperature in the range 500~800°C.



Fig. 2. Reaction chamber used for nitriding tests.

After each solar irradiation test run for specified duration, NH_3 gas flow was substituted with N_2 gas at comparatively fast flow rate 60 L/h to substitute NH_3 gas in the reaction chamber in 5 min in order to avoid undesired loss of N from the nitrided specimens during cooling in NH_3 gas flow that would act as hydriding agent at relatively low temperature [16]. Reaction products were identified by XRD analysis done using a Geigerflex D/MAC IIC diffractometer of RIGAKU with $\text{CuK}\alpha$ radiation over a scan range of 2θ from 30° to 140° at a scanning speed of $2^\circ/\text{min}$ with a step of 0.012° . Phase identification was done referring to the ICDD (International Center for Diffraction Data) card data compiled by JCPDS (Joint Committee on Powder Diffraction Standards).

3. Results and Discussion

Table 2 summarizes the measured values of initial mass m_i and final mass m_f of V and Nb samples exposed at 600, 700 and 800°C for 90 min, as well as the corresponding relative mass gains $\Delta m/m_i$ calculated ($\Delta m = m_f - m_i$). In the case of Ta, it was not possible to determine mass changes owing to disintegration (pulverization) of the samples during irradiation to concentrated solar beam in stream of NH_3 gas. It should be noted that if nitriding proceeded to stoichiometric composition MN, $\Delta m/m_i$ would be 0.275 for V, 0.151 for Nb and 0.077 for Ta as listed in Table 1 in [9]. This was obviously not the case as seen in Table 2 suggesting that only partial nitridation took place, which is not surprising in view of the fact that compacted pellets rather than loose powders were

used. The option of using compacted pellet sample in place of loose powder form of sample materials was taken in this work in order to avoid cross-contamination among specimen materials and to test as many samples possible at once within the limit of provided solar beam time for respective users.

Table 2. Detected mass changes after 90 min at different processing temperature T for V and Nb.

600°C - E03			
	m_i (g)	m_f (g)	$\Delta m/m_i$
V	0.6936	0.7253	0.0457
Nb	0.9744	0.9866	0.0125
700°C - E01			
	m_i (g)	m_f (g)	$\Delta m/m_i$
V	0.7032	0.7714	0.0682
Nb	0.9819	1.0016	0.0197
800°C - E07			
	m_i (g)	m_f (g)	$\Delta m/m_i$
V	0.8001	0.9207	0.1206
Nb	1.1499	1.1818	0.0319

3.1. Vanadium (V)

XRD patterns observed for top surfaces of V specimen pellets are reproduced in Fig. 3.

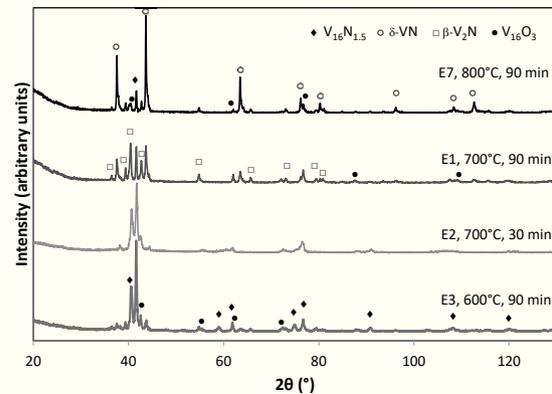


Fig. 3. XRD patterns of V after reaction with uncracked NH_3 .

No trace of metallic V was detected by XRD on the surface of V pellets treated in stream of NH_3 gas over temperature range between 600 and 800°C. At 600°C, XRD peaks identifiable as tetragonal $\text{V}_{16}\text{N}_{1.5}$ was detected. This phase must be a primary solid solution phase of N in metallic V lattice that might be represented by V(N). At 700°C after 90 min reaction, sub-nitride V_2N was dominant over the pellet top

surface with traces of mono-nitride VN and oxide identified as $V_{16}O_3$ (ICDD 01-075-6708) that might be represented as V(O) like $V_{16}N_{1.5}$ to be represented as V(N) whereas, at 800°C, dominant phase became mono-nitride δ -VN with traces of β - V_2N and $V_{16}O_3$.

3.2. Niobium (Nb)

XRD patterns observed for top surface of the Nb pellet specimens are reproduced in Fig. 4.

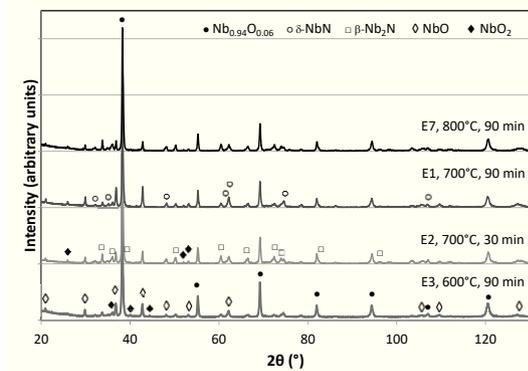


Fig. 4. XRD patterns of Nb after reaction with uncracked NH_3 .

At 600°C after 90 min reaction (run E3), XRD peaks identified were oxides, NbO (ICDD 01-071-2146) and NbO_2 (ICDD 00-034-0898), besides those identifiable as primary solid solution $Nb_{0.94}O_{0.06}$ (ICDD 01-074-6000) that might be represented as Nb(O). At 700°C, XRD peaks identifiable as NbO_2 , and NbO and Nb(O) were detectable after 30 min reaction but, after prolonging the reaction duration to 90 min, sub-nitride phase β - Nb_2N became also detectable. By prolonging the reaction duration to 90 min (run E1) from 30 min (run E2) at 700°C, extent of nitridation of Nb appeared to advance further yielding diminished extent of oxidation. This trend might be interpreted in terms of advanced removal of oxygen in form of H_2O from Nb surface that was initially covered with oxide layer by action of H possessing high $a(H)$ in the flowing NH_3 gas. By raising the reaction temperature to 800°C (E7) from 700°C (E1) for reaction period 90 min, XRD patterns in Fig. 4 did not appear to change appreciably. Thus, optimum nitridation temperature for Nb under the given condition of NH_3 gas flow rate might be claimed to be 700°C.

3.3. Tantalum (Ta)

XRD patterns observed for top surfaces of Ta specimen pellets are reproduced in Fig. 5. As already

mentioned earlier in the text, Ta specimens underwent pulverization during test runs at any chosen reaction temperature T in the range 600~800°C, XRD patterns reproduced in Fig. 5 were taken for pulverized reaction products from Ta whereas XRD patterns for V and Nb specimens reproduced in Fig. 3 and Fig. 4, respectively, were taken at the specimen top surface.

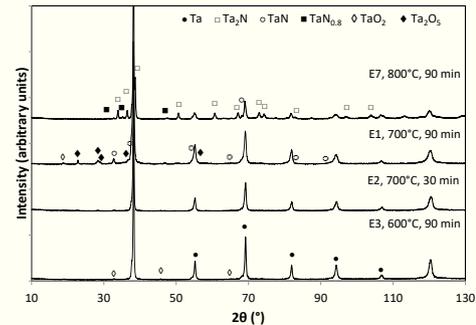


Fig. 5. XRD patterns of Ta after reaction with uncracked NH_3 .

As seen in Fig. 5, by the processing at $T = 600^\circ C$, metallic Ta remained as the dominant phase associated with weak peaks identifiable as TaO_2 but showing no evidence of nitride formation even after 90 min (E3). At $T = 700^\circ C$ after 30 min (E2), XRD pattern looked largely comparable to that of the Ta specimen processed at 600°C for 90 min (E3). However, when the exposure time at 700°C was increased from 30 min (E2) to 90 min, trace of TaN (ICDD 01-079-5780) became detectable besides Ta_2O_5 (ICDD 01-070-9177) (E1). Anyway, XRD peak intensity of TaN phase in the E1 specimen was too weak to become discernible in Fig. 5 although corresponding peak positions are recognizable in the digitalized XRD record. At 800°C, two nitride phases of Ta, Ta_2N (ICDD 00-026-0985) and TaN (ICDD 01-079-5780), became detectable.

A few remarkable aspects are noticed in Fig. 5. One of them is dominant presence of metallic Ta in the E3 specimen implying that surface oxide layer covering Ta powders initially were reduced by the action of high $a(H)$ of flowing NH_3 [13,16] although nitriding did not proceed at 600°C. At 700°C after 90 min, TaN phase became detectable (E1) while Ta_2N became more abundant at 800°C after 90 min (E7). Difference in nitride phase constitution between E1 and E7 test runs might be appreciated rationally in terms of progressed extent of NH_3 dissociation to lead to lower $a(N)$ at 800°C (E7) than at 700°C (E1).

On synthesizing Ta carbide under co-existence of excess free carbon under heating with concentrated

solar beam to 1600°C, Ta₂C was formed after 30 min although thermodynamic equilibrium phase in Ta-C system is TaC under the chosen condition and it took 90 min to fully convert the reaction product to TaC co-existing with free C [17]. Similarly, formation of Ta₂N preceded to formation of TaN in our earlier attempt of synthesizing nitride in N₂ gas under solar radiation heating to 2000°C [18].

4. Concluding Remarks

As pointed out earlier in the text, nitride of Va-group metals (V, Nb and Ta) might be synthesized in N₂ gas environment at *T* higher than 1500 K and thence there is no absolute necessity to use flowing NH₃ gas as the nitriding medium for Va group metals. However, pragmatic merits of using uncracked NH₃ as the nitriding medium include diminished reaction temperature and reduced reaction duration that are quite attractive in modern era of rising global concern over sustainable development with efficient usage of energy and resources.

Nitrides and carbides of transition metals are now considered as unique functional materials besides conventional refractory applications [5-7]. But synthesis of superconductive MoN, for example, would require very high pressure and temperature in expensive autoclave reactor [6]. As an alternative synthesis method of ceramic nitride, combustion synthesis (CS) processing also known as SHS (self-propagating high-temperature synthesis) is intensively investigated [5]. For SHS, merits of pre-mixing metal powders with preliminary nitrided powders as diluent in starting materials are systematically reviewed [5].

The reaction products synthesized from powders of Va-group metals in flowing NH₃ gas under heating with concentrated solar beam up to 800°C in short period up to 90 min were consisted of mixture of MN and M₂N and they might not be accepted as final industrial product but they might be used as starting material to be processed further by conventional industrial process or SHS for final industrial product. Further efforts must be invested to elucidate effect of extent of dissociation of NH₃ gas on the reaction product by systematically changing NH₃ gas flow rate under the solar irradiation experiment to find out optimum conditions of synthesizing nitride product possessing demanded quality.

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