LOW-TEMPERATURE NITRIDING OF VA-GROUP METAL POWDERS (V, Nb, Ta) IN FLOWING NH_3 GAS UNDER HEATING WITH CONCENTRATED SOLAR BEAM AT PSA

J.C. Fernandes[1], F.A.C. Oliveira[2], L. G. Rosa[1], J. Rodríguez[3], I. Cañadas[3], T. Magalhães[2], N. Shohoji[2,*]

[1] IST - Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal
[2] LNEG - Laboratório Nacional de Energia e Geologia, LEN - Laboratório de Energia, Estrada do Paço do Lumiar, 1649-038 Lisboa, Portugal
[3] CIEMAT - Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas, PSA - Plataforma Solar de Almería, Ctra. Senés Km. 4, P.O. Box 44, 04200, Tabernas, Almería, Spain
[*] corresponding author: nobumitsu.shohoji@lneg.pt

Keywords: Synthesis, Nitridation, Tantalum nitrides, Concentrated Solar Energy, Ammonia

Abstract

Over the last two decades, we 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 gas. In recent works [1,2] nitriding of VIa-group metals (Cr, Mo, W) and Fe in stream of NH_3 gas with suppressed extent of dissociation (uncracked NH_3) was attempted under heating with concentrated solar beam. It was demonstrated that mono-nitride δ-MoN of Mo and sub-nitride ε-Fe_2N of Fe that are known to be impossible to synthesize in N_2 gas environment even at elevated pressure $p(N_2)$ were successfully synthesized by the reactions of these metals in stream of NH_3 gas under heating with concentrated solar beam up to 800ºC.
In the present work, nitriding of Va-group metals (V, Nb and Ta) was attempted in stream of NH_3 gas under irradiation of concentrated solar beam. By up to 90 min heating in uncracked NH_3 under concentrated solar beam up to 800ºC, reaction products were identified by X-ray diffraction (XRD) analysis to be consisted of mono-nitride MN co-existent with sub-nitride M_2N.

1. Introduction

The nitrides of d-group transition metals are refractory hard metals with significant industrial importance. Of particular interest is the special nature of their electrical properties making them suitable for electronic devices as mentioned in our earlier publication [1].
Synthesis of refractory nitrides is usually carried out at temperatures higher than 1500ºC in N_2 gas and, thus, it is a highly energy-consuming process. In recent works [1,2], the authors demonstrated that nitrides of Fe and VIa-group metals might be synthesized under stream of NH_3 gas under irradiation with concentrated solar beam like in conventional electric furnace. For Va-group metals (V, Nb, Ta), synthesis of mono-nitride MN might be realized in N_2 gas environment and thence, unlike for Fe and VIa-group metals, there is no absolute necessity of using uncracked NH3 as a nitriding agent. However, the authors thought that it might be pragmatic technical convenience to check possibility of formation of nitride in uncracked NH3 under heating with concentrated solar beam in view of energy saving.

2. Experimental

The powders of Va-group metals (V, Nb and Ta) were compacted in form of pellets and nitridation reactions were carried out in the PSA vertical axis solar furnace SF5 [3]. The experimental details can be found elsewhere [1,2]. Phases existing in the reaction products obtained were identified by XRD analysis.

3. Results and discussion

As demonstrated by XRD analysis, reaction products were consisted of mono-nitride MN co-existent with

sub-nitride M_2N in spite of relatively low reaction temperature used (a typical example for Ta pellets is shown in Fig. 1). Due to demand for maintaining extent of dissociation of flowing NH_3 gas at a satisfactorily low level to gain high nitrogen chemical activity a(N) of uncracked NH_3, it is preferable to use temperature not exceeding 1000ºC. Below 700ºC, only slight nitridation of the Ta powders has occurred.When the exposure time at 700ºC was increased from 30 min to 90 min, traces of TaN (ICDD card n. º 079-5780), were formed. At 800ºC, two nitride phases, Ta_2N (ICDD card n.º 026-0985) and traces of TaN were synthesised suggesting that a(N) was not high enough to form single-phase or reaction duration was not sufficiently long to fully convert Ta_2N to TaN. Similar diffraction patterns (not shown) were observed for V and Nb. This aspect has to be elucidated by future experimental work.

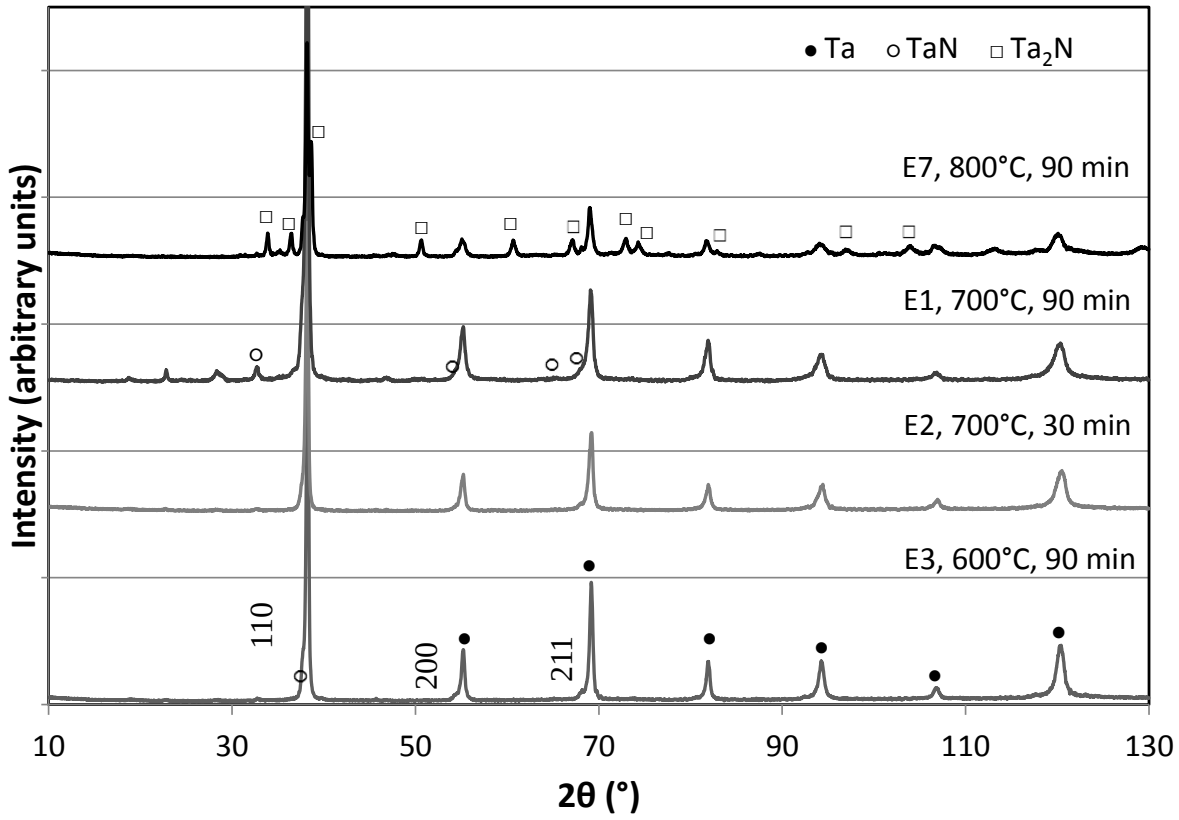

Fig. 1 XRD patterns showing the reaction products obtained.

4. Conclusions

From the present study, the following conclusions could be drawn:
- Partial nitridation of Va-group metal powders consisting of a mixture of mainly M_2N and traces of MN was achieved at 800ºC under flowing NH_3 (10 l/h) and solar heating upon 90 min exposure.
- Such mixture of MN and M_2N of Va-group metals might be used as precursor for MN synthesis of controlled N/M ratio by eventual nitriding in N_2 gas environment with controlled $p(N_2)$ and temperature T.

References

[1] N. Shohoji, F.A.C. Oliveira, J.C. Fernandes, L.G. Rosa, J. Rodríguez, I. Cañadas, C. Ramos, T. Magalhães, F. Cestari, Synthesizing higher nitride of molybdenum (Mo) and iron (Fe) in ammonia (NH_3) gas stream under irradiation of concentrated solar beam in a solar furnace, Materialwissenschaft und Werkstofftechnik 44 (2013) 959-971.
[2] F.A.C. Oliveira, L.G. Rosa, J.C. Fernandes, J. Rodríguez, I. Cañadas, T. Magalhães, N. Shohoji, Nitriding VIa-group metals (Cr, Mo and W) in stream of NH_3 gas under concentrated solar irradiation in a solar furnace at PSA (Plataforma Solar de Almería), Solar Energy (SE_4267) in press.
[3] J. Rodríguez, I. Cañadas, E. Zarza, PSA vertical axis solar furnace SF5, Energy Procedia 49 (2014) 1511-1522.