



The effect of low levels of dopants upon the formation and properties of beta-phase molybdenum nitride

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ABSTRACT

The addition of 1 wt% Pd, Au, Ni and Cu dopants has been demonstrated to strongly alter the morphology of beta-phase molybdenum nitride prepared by treatment of MoO₃ with a 3/1 H₂/N₂ mixture at 750 °C. Furthermore, the addition of Pd significantly enhances the surface area and the formation of the nitride phase. It is proposed that the facile formation of molybdenum bronzes in this system is important in this respect. The dopants have also been observed to modify the denitridation characteristics of the beta-phase, with an overall reduction of the proportion of NH₃ formed upon using a 3/1 H₂/Ar mixture with respect to the undoped sample.

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1. Introduction

Metal nitrides and oxynitrides continue to attract attention as heterogeneous catalysts [1–3]. To date, many studies have centred upon the perceived analogies of the catalytic efficacy of some transition metal interstitial nitrides with that of noble metals. Interest in oxynitride systems has largely concerned their application in base catalysis, e.g. [4,5]. Recently, much attention has also been paid toward the application of nitrogen doped oxides, in particular titania, as visible light active photocatalysts, e.g. [6,7]. Our interest in nitrides is predominantly directed towards the possibility that they may function as nitrogen transfer agents in which nitrogen can be removed and reloaded in separate reaction steps. This idea can be related to the Mars–van Krevelen mechanism, in which the lattice oxygen species of a metal oxide are the active oxidant in oxidation catalysis over metal oxides subsequently being replenished from a gas-phase oxygen source, which is well established [8,9]. Analogous processes are also known to occur in systems involving sulfur transfer with sulfides [10] and carbon transfer with carbides [11]. In terms of nitrides, we have reported our studies

on the Co₃Mo₃N system [12–14], in which we have shown that 50% of the lattice nitrogen species can be removed to generate the unprecedented Co₆Mo₆N phase, in which residual nitrogen relocates from the 8a to 16c Wyckoff site [14,15].

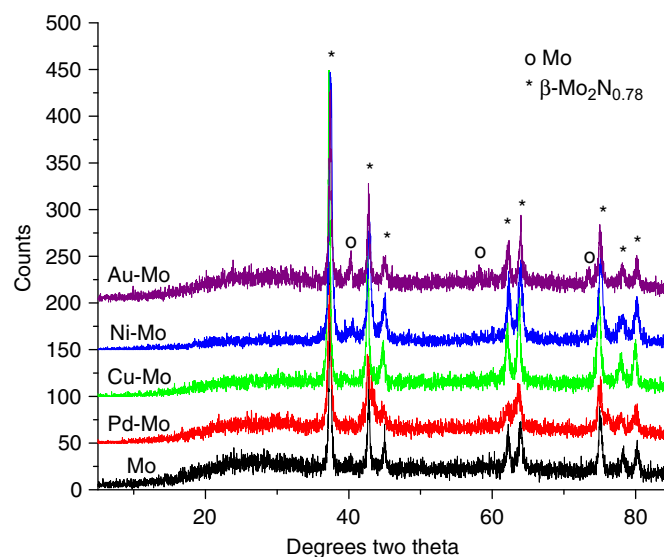


Fig. 1. Powder X-ray diffraction patterns of nitrided samples.

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In the current manuscript, we detail our investigations of metal doped beta-phase molybdenum nitride, paying particular attention to their denitridation characteristics. These systems have been chosen to illustrate the effect of the inclusion of low levels of metal dopants, which could be anticipated to exert significant influence over the beta-nitride both in terms of hydrogen spillover behaviour and electronic modification via, for example, Schottky barrier effects. Beta-phase molybdenum nitride has been selected for investigation because of its ease of preparation, which involves treatment of a MoO_3 precursor under

a 3:1 mixture of $\text{H}_2:\text{N}_2$ at elevated temperature, although caution must be exercised to avoid the formation of molybdenum metal, as observed in powder X-ray diffraction patterns under some circumstances [16]. However, to date, a number of different stoichiometries for the beta-phase have been reported [17–21] and the location of nitrogen in the lattice does not seem to be well defined. These aspects, which are currently undergoing further investigation within our research group, may be related to the fact that variable composition is evident in the phase diagram [22].

2. Experimental

Doped materials were prepared by impregnation. For this purpose, the required amount of nitrate (Ni, Cu or Pd), previously dissolved in a small amount of water, was added to MoO_3 (Sigma–Aldrich, 99.5%). In the case of Au, the precursor HAuCl_4 was first dissolved in water and the required amount was added to the MoO_3 powder. The sample was then dried overnight at 120°C and finally calcined in air at 500°C for 5 h. The undoped sample, used as a reference, was prepared by immersion of the MoO_3 in water,

Table 1
Nitrogen content and BET surface area of molybdenum nitride samples.

Dopant	Nitrogen content (wt%)	Surface area ($\text{m}^2 \text{g}^{-1}$)
Undoped	5.24	7.3
Au	4.30	6.3
Cu	5.55	7.9
Ni	5.60	10.4
Pd	4.88	30.0

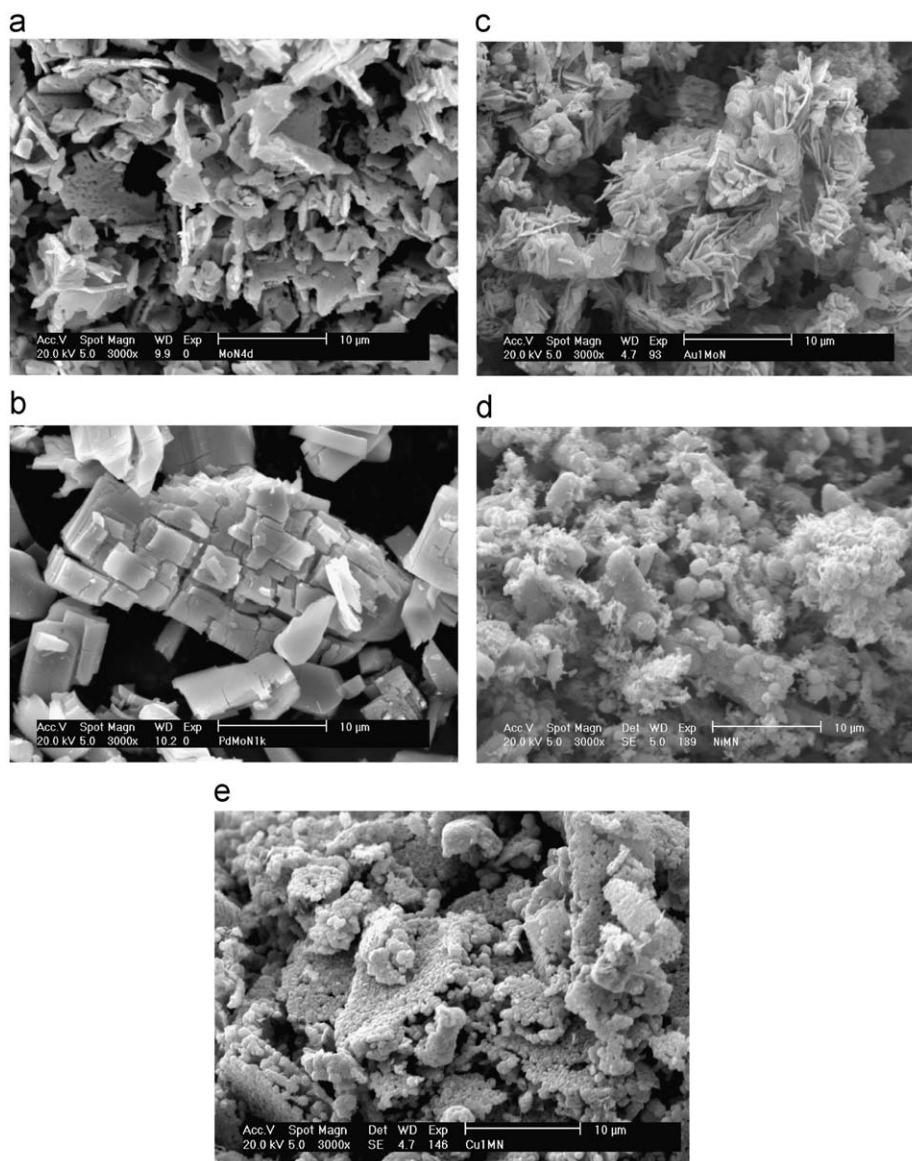


Fig. 2. SEM images of nitrided samples: (a) undoped, (b) 1 wt% Pd doped, (c) 1 wt% Au doped, (d) 1 wt% Ni and (e) 1 wt% Cu.

following by drying and calcination as for the doped samples. All precursors contained 1 wt% of metal (Au, Pd, Ni or Cu) on MoO₃. The synthesis of the β -molybdenum nitride was performed in a quartz microreactor. For this purpose approximately 0.4 g of MoO₃ or MoO₃ doped with metal, was placed between two plugs of quartz wool in a tubular quartz reactor. The reactor was first purged and then heated up from ambient temperature to 750 °C, under a dry 3:1 H₂/N₂ gas mixture, (60 ml min⁻¹, BOC). The temperature ramp applied was 10 °C min⁻¹ and samples were held at 750 °C for 3 h prior to cooling back to ambient temperature under the H₂/N₂ flow. Subsequently, following passivation by back-diffusion of air into the reactor system, the samples were discharged from the reactor and characterized by various techniques. Another set of experiments was also performed with the aim to remove the nitrogen from the lattice of the molybdenum nitride. For this purpose the samples were first nitrated as described and the reactor was then cooled down to 400 °C under N₂/H₂ at which point the gas feed was switched to dry H₂/Ar (3:1, 60 ml min⁻¹, BOC). The system was held at 400 °C for 1 h prior to being sequentially increased to 500, 600, 700 and 750 °C, with a 1 h dwell time at each temperature. The formation of NH₃ was determined by the change in conductivity of a standard sulfuric acid solution through which the effluent gases were passed. Following these measurements, the system was subsequently cooled down to room temperature under the flow of H₂/Ar. The samples were then discharged from the reactor for further characterization. All samples were characterized by powder X-ray diffraction (XRD) using a Siemens D5000 diffractometer with CuK α radiation. In these measurements a 2 θ range between 5° and 85° was scanned using a counting rate of 1 s per step with a step size of 0.02°. Furthermore, in order to study the morphological features, SEM images were taken using a XL30 ESEM Philips microscope operating at 20 kV. The surface areas were determined by N₂ physisorption at 77 K applying the BET method. Physisorption studies were performed with a Micromeritics Gemini instrument. CHN determination was performed using an Exeter Analytical CE-440 elemental analyser.

It should be noted that the contact of gold with ammonia can lead to explosion (“fulminating gold”), and so extreme caution is urged when dealing with gold containing materials under environments which either contain, or can potentially produce, NH₃ [23].

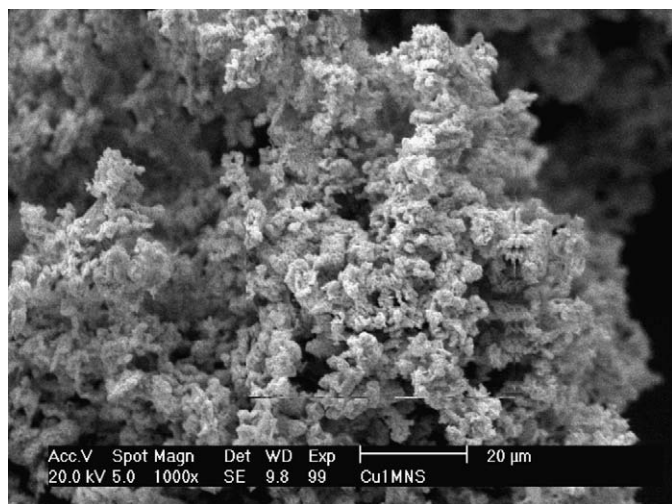


Fig. 3. SEM image of 1 wt% copper containing nitrated sample prepared using copper sulphate as dopant.

3. Results

Fig. 1 presents powder X-ray diffraction patterns of the materials after nitridation. In all cases, the major phase can be indexed to beta-molybdenum nitride, as expected for the nitridation conditions employed [16]. Very low levels of molybdenum metal, most easily seen from its signature reflection at ca. 40.5° 2 θ , can also be observed in most of the samples. In the doped samples, given the small quantity of additive, it is not surprising that no additional phases associated with the dopant are evident. The nitrogen content of samples has been determined by CHN analysis and the data are presented in Table 1. If the stoichiometry of the beta-phase is assumed to be Mo₂N_{0.78}, as is commonly reported in the literature [20,21], the nitrogen content of the pure phase would be expected to be 5.38 wt%. It is notable that nitrogen content of most of the samples is close to, or even exceeds, this value indicating that a high level of nitridation has been achieved. However, the nitrogen contents of the palladium and, in particular, the gold doped

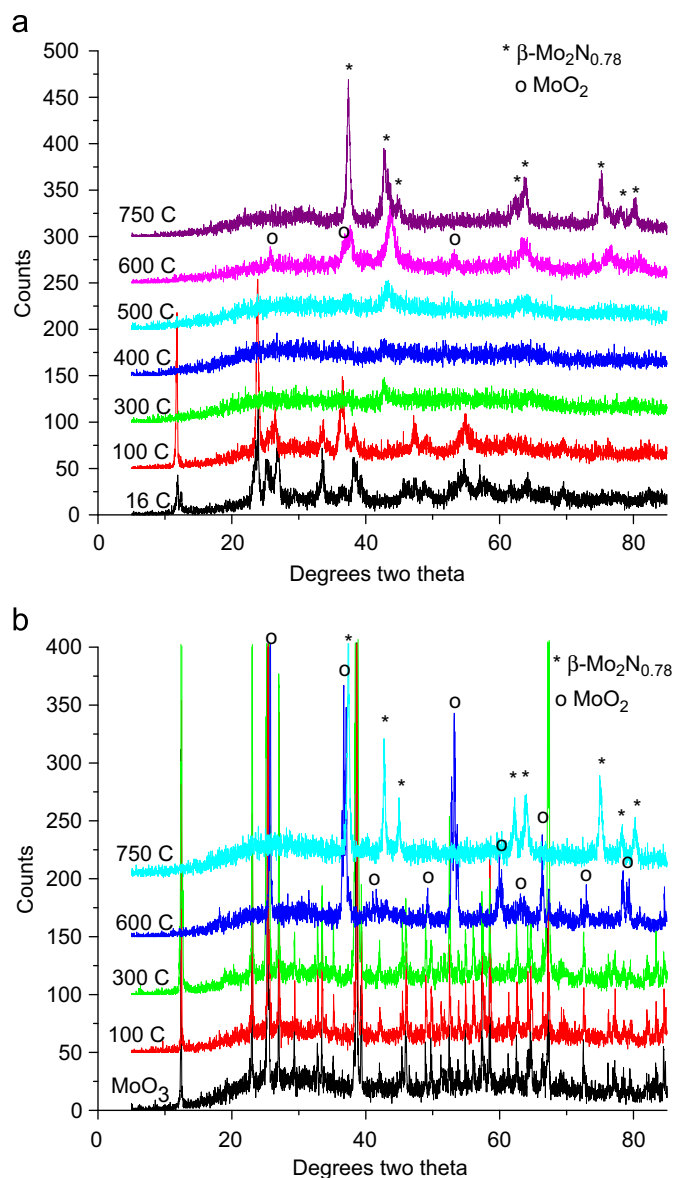


Fig. 4. Powder X-ray diffraction patterns of MoO₃ samples exposed to the 3/1 H₂/N₂ nitriding mixture at various temperatures for 3 h: (a) 1 wt% Pd doped sample and (b) undoped sample.

samples are significantly below this value. In these cases, it is possible to advance alternative contrary explanations. Upon discharge of the palladium sample from the reactor, it was observed that the sample can spark and a strong exotherm can result unless care is taken to ensure that the sample has been fully passivated prior to removal. *Consequently, caution must be exercised concerning the discharge of palladium samples.* Therefore the probable explanation for the lower nitrogen content is oxidation subsequently to the formation of the nitride phase, although it is notable that complete oxidation does not occur and a significant amount of nitrogen is still present in the material as apparent from the CHN data and its XRD pattern. In the case of the gold doped sample, the explanation appears different—no such exotherm occurs. In this case, we propose that the low level of gold present retards the formation of the nitride phase. It is notable that the signature reflections of Mo metal are more prominent in the diffraction pattern of this sample.

Table 2

Nitrogen content and BET surface area of undoped and 1 wt% Pd doped MoO₃ as a function of pre-treatment temperature under 60 ml min⁻¹ 3/1 H₂/N₂ for 3 h.

Sample/pre-treatment temperature	Nitrogen content (wt%)	Surface area (m ² g ⁻¹)
MoO ₃ /16 °C	0	< 0.5
MoO ₃ /100 °C	0	< 0.5
MoO ₃ /300 °C	0	1.0
MoO ₃ /600 °C	0.73	1.0
MoO ₃ /750 °C	5.24	7.3
Pd/MoO ₃ /16 °C	0	0.6
Pd/MoO ₃ /100 °C	0	1.8
Pd/MoO ₃ /300 °C	0	0.6
Pd/MoO ₃ /400 °C	0	< 0.5
Pd/MoO ₃ /500 °C	0	0.7
Pd/MoO ₃ /600 °C	2.19	89.6
Pd/MoO ₃ /750 °C	4.88	30.0

SEM has been applied to determine the morphology of samples and the results are presented in Fig. 2, where it can be seen that the metal dopants have a strong influence upon the morphology of the resultant beta-nitride samples. Consistent with previous observations [13,16], the undoped sample comprises flake like morphology particles. Porosity can be observed in some crystallites which may occur as a consequence of the elimination of water during the transformation process, as we have described elsewhere [16]. The inclusion of 1 wt% Pd dramatically changes this, leading to highly faceted crystallites which exhibit fractures. As discussed, it is possible that this sample experiences a strong exotherm leading to this morphology upon passivation. However, given the fact that the powder diffraction and CHN data evidence that the sample is not completely oxidized, the extent of this effect must be limited. The occurrence of the fractures may be as a result of associated thermal stresses occurring after exposure to N₂/H₂ or the change in sample density upon transformation. Gold (1 wt%) also has a strong effect upon morphology. In this case, the formation of flake-like crystals which are finer than those evident in the undoped beta-phase sample is evident. In the case of 1 wt% Ni, yet another morphology is evident with the SEM investigations evidencing mixed shapes with some spherical crystallites being observed. The most striking dopant effect is observed in the case of 1 wt% Cu. In this sample a “sandwich-like” morphology is observed in which large layer structures comprised of aggregates of smaller crystallites are paired together forming interlayer spaces which contain additional smaller crystallites. SEM observations confirmed that the morphological differences were not evident in the pre-nitrided samples which indicates that they arise as a consequence of the nitridation procedure. At present, the exact mechanism by which such low levels of different dopants exhibit pronounced and distinct influence upon morphology remains unclear. One possible explanation lies in the different efficacies of metal ion dopants for hydrogen activation. In this way, via the spillover

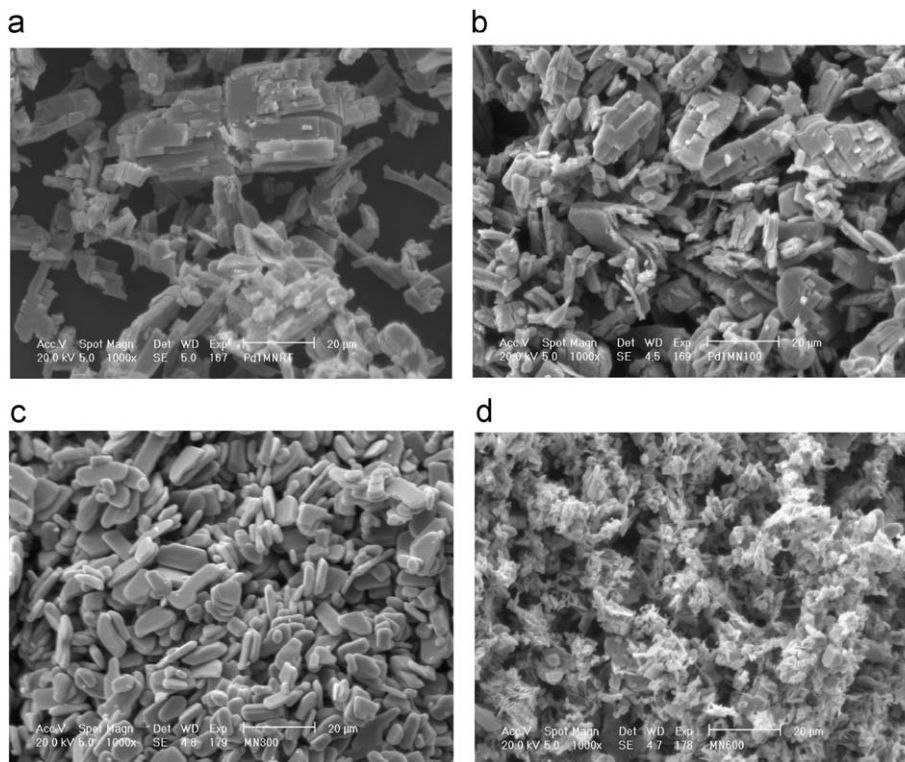


Fig. 5. SEM images of MoO₃ samples exposed to the 3/1 H₂/N₂ nitriding mixture at various temperatures for 3 h: (a) 1 wt% Pd pretreated at 16 °C, (b) 1 wt% Pd pretreated at 300 °C, (c) undoped sample pretreated at 300 °C and (d) undoped sample pretreated at 600 °C.

of activated hydrogen, it is possible that the temperatures at which the various reduction and transformation steps in the conversion of MoO_3 to beta-molybdenum nitride differ within each sample. This could also have the result that the water generated is present at differing stages (and temperatures) in the transformation sequence for the different samples, which could be determining for the morphology exhibited. However, consideration of the possible effect of the dopant anion should also be made. In the present study, with the exception of Au, nitrate salts have been used as dopant which minimizes the potential impact of this effect within the current study, although the absolute amount of nitrate anion will differ between the various samples. In order to illustrate the effect of dopant anion upon morphology, 1 wt% Cu from a copper sulfate precursor has been doped onto MoO_3 and the resultant beta-phase nitride has been prepared using the same conditions as for the other samples investigated in this study. Fig. 3 presents a representative SEM micrograph for this sample and it can be seen that the resultant morphology differs from the corresponding sample prepared employing the nitrate precursor. Possible explanations for this observation also relate to differences in reduction/transformation temperature as well as effects of the pH of the dopant solution. The variation of morphology is an important observation, which is likely to have major impact on catalysis in the case of structure-sensitive reactions, even in the absence of additional effects deriving from the presence of the dopants. Accordingly, the effects of dopant upon morphology are currently undergoing further investigation.

The influence of dopant upon BET surface area has been investigated and the results are presented in Table 1. The surface areas of the oxide precursors are very low ($< 1.5 \text{ m}^2 \text{ g}^{-1}$) and that the presence of dopant does not produce any significant effect. Upon nitridation, surface areas are observed to increase, and with the exception of palladium and also possibly nickel, are not strongly influenced by dopant despite the differences in morphology. Although not particularly large, it is evident that the surface area of the palladium doped sample is significantly greater than that of the other nitrides. In this respect, it is interesting to draw comparisons with the literature describing the influence of transformation pathway on the formation of $\gamma\text{-Mo}_2\text{N}$ by ammo-

lysis of MoO_3 . [24,25]. In this method, high space velocities and carefully controlled temperature ramp rates are applied to maximize surface area by minimizing sintering [26]. Unlike the formation of the beta-phase nitride, ammonolysis leads to $\gamma\text{-Mo}_2\text{N}$ which is pseudomorphic with the MoO_3 precursor which is generated by a topotactic pathway [26]. Studies of the influence of reaction variables in this system have indicated that the surface area of the resultant nitride is enhanced if molybdenum bronzes (H_xMoO_3) are intermediates in the transformation sequence [24]. It has been argued that the transformation sequence is different in the case of the beta-phase molybdenum nitride generated by the reaction of MoO_3 with H_2/N_2 mixtures, with MoO_2 and Mo metal being pivotal intermediates [27]. Interestingly, in another context, it has been established that the presence of precious metal dopants on MoO_3 can lead to the facile formation of molybdenum bronzes at ambient temperature [28] in which hydrogen activation precedes the rapid migration [29] of spilt over hydrogen atoms into the interlayer spacing of MoO_3 where OH and OH_2 groups can be formed [30]. Accordingly, it is possible that molybdenum bronzes occur as intermediates in the case of Pd doped MoO_3 in the formation of the beta-phase nitrides. Consequently, this was investigated and it was observed that contacting the Pd/ MoO_3 precursor with the H_2/N_2 mixture at ambient temperature (in this case 16°C) led to a rapid transformation (complete in under 2 min) accompanied with a change in colour of the sample from chocolate brown to dark blue/black, indicative of the formation of H_xMoO_3 . XRD analysis of the resultant sample (Fig. 4) evidences the formation

Table 3
Nitrogen content and BET surface area of denitrated samples.

Dopant	Nitrogen content (wt%)	Surface area ($\text{m}^2 \text{ g}^{-1}$)
Undoped	0	5.2
Au	0.75	2.6
Cu	0	4.7
Ni	0	2.9
Pd	1.23	14.9

Table 4
Ammonia production as a function of temperature.

Dopant	400 °C ^a	500 °C ^a	600 °C ^a	700 °C ^a	750 °C ^a	Total NH_3 production ^b	% lattice nitrogen lost as NH_3 ^c
undoped	–	1.02	9.49	9.49	–	20.00	13.0
Au	1.68	–	1.02	9.49	5.84	18.03	11.7
Cu	1.75	0.22	1.24	1.02	0.73	4.96	3.2
Ni	1.46	1.97	0.80	1.10	1.46	6.79	4.4
Pd	3.58	0.66	0.80	–	0.58	5.62	3.7

^a 10^5 mol NH_3 produced/h.

^b Over the entire temperature range.

^c Assuming that the stoichiometry corresponds to 5.38 wt%.

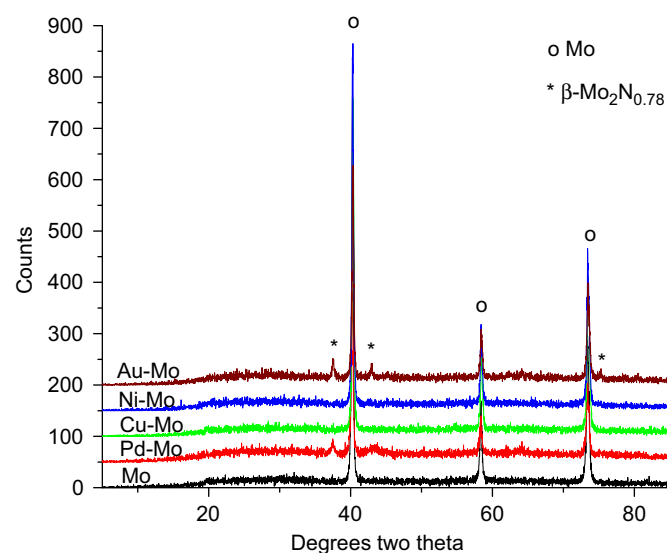


Fig. 6. Powder X-ray diffraction patterns of samples following denitridation.

of molybdenum bronze(s). It is possible to fit the pattern with the combination of a number of molybdenum bronze phases of different stoichiometry— $\text{H}_{0.34}\text{MoO}_3$ (JCPDS 034-1230), $\text{H}_{0.93}\text{MoO}_3$ (JCPDS 033-0605) and $\text{H}_{1.68}\text{MoO}_3$ (JCPDS 033-0604). A number of subsequent experiments were carefully undertaken to determine whether the facile activation of hydrogen in this system could lead to a reduction in the temperature at which the beta-molybdenum nitride phase was formed. Pd/MoO_3 was treated with H_2/N_2 at various temperatures for 3 h, after which the sample was cooled to ambient temperature, allowed to slowly passivate and was investigated by XRD and CHN analysis. As can be seen in Fig. 4, molybdenum bronzes are the product of reaction at low reaction temperatures. However, at 300 and 400 °C, the sample becomes generally amorphous. Features related to those expected in the beta-nitride begin to emerge and get stronger with increasing temperature. The CHN analysis presented in Table 2 indicates that the materials prepared at 600 °C are oxynitrides and the incorporation of nitrogen increases as a function of temperature. The surface area for the Pd doped sample shows an interesting trend passing through a maximum at the intermediate oxynitride stage. SEM investigations of the resultant samples produced at various intermediate temperatures are

presented in Fig. 5. It can be seen that the highly faceted morphology complete with the fractures observed in the corresponding precursor subjected to higher reaction temperature is formed during ambient temperature treatment. Consequently, since at this stage the major form of this material is molybdenum bronze(s), it can be concluded that the morphology for this sample is not solely related to the nitride phase. As expected, it can be seen that this morphology is retained at intermediate temperatures, although at this stage the material exhibits an amorphous diffraction pattern, despite its crystalline appearance. In order to directly elucidate the influence of the Pd dopant upon the transformation process, a series of parallel experiments were undertaken on undoped MoO_3 . The XRD results, presented in Fig. 4, illustrate that the transformation occurs via a different route, with MoO_3 being stable to fairly high temperatures. At 600 °C, although some reflections resembling those of the beta-molybdenum nitride phase appear to be present, but the corresponding nitrogen analysis indicates the nitrogen content of this material to be very low (Table 2), further confirming the strong promotion of the Pd dopant upon the formation of the nitride phase by comparison. The influence exerted by palladium is interesting, since it may indicate that

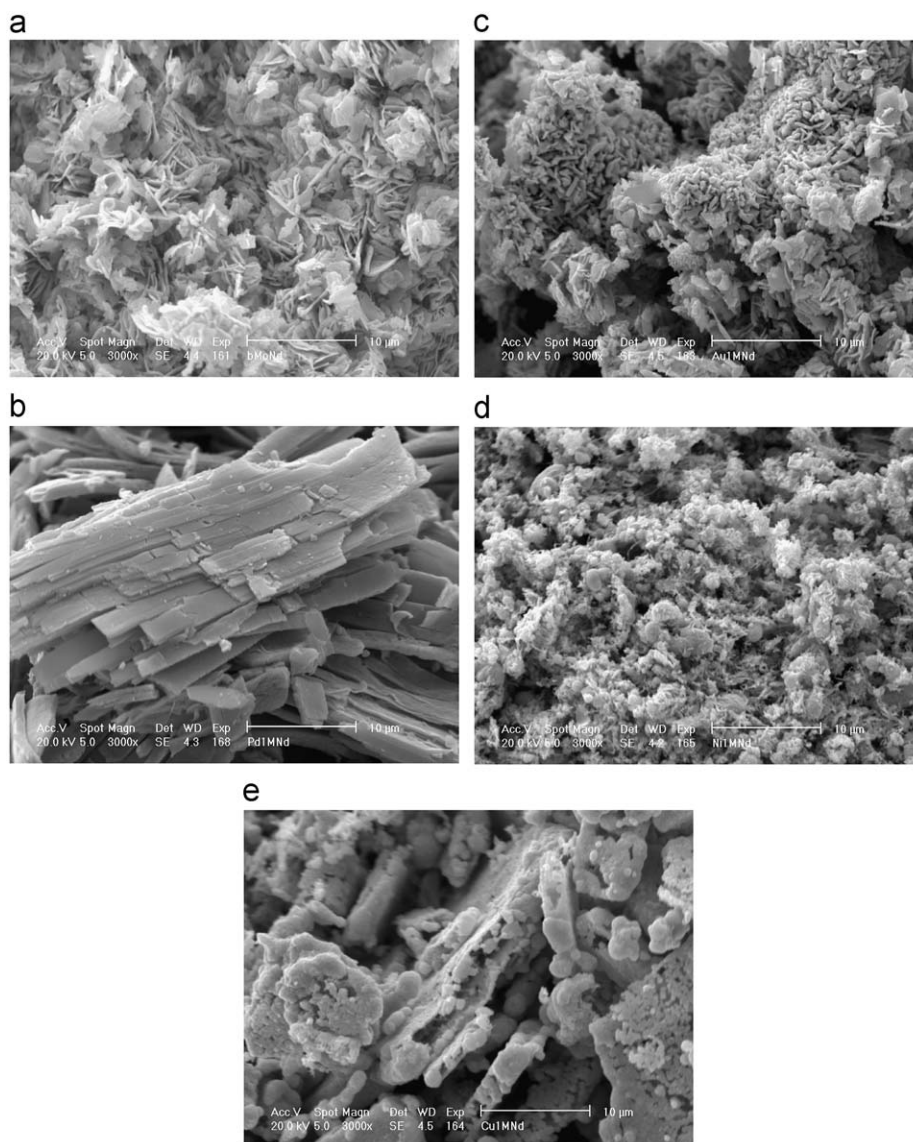


Fig. 7. SEM images of samples following denitridation: (a) undoped, (b) 1 wt% Pd doped, (c) 1 wt% Au doped, (d) 1 wt% Ni and (e) 1 wt% Cu.

it is the activation of hydrogen, rather than nitrogen, which is determining for the temperature of transformation. SEM characterization of the undoped MoO₃ as a function of pretreatment temperature is also shown in Fig. 5. The morphology observed at 300 °C reflects that of the precursor, whereas at 600 °C it more closely resembles that of the beta-phase nitride.

In order to assess the reactivity of lattice nitrogen and the influence of doping upon it, the evolution of NH₃ was measured using temperature programmed reaction with Ar/H₂ in the range 400–750 °C, with a 60 min dwell time at each temperature. The results are presented in Table 4. It can be seen that all metal dopants reduce the production of ammonia to different extents. The profile of ammonia production as a function of temperature is also affected. For example, despite the fact that Pd exhibits a strong inhibition for the production of NH₃, it enhances the production of NH₃ at 400 °C, which could relate to the desorption of surface NH_x residues particularly as this sample possesses the highest surface area of those investigated. Consistent with this, in a study of γ -Mo₂N, Wei and co-workers [31] evidenced two forms of adsorbed NH_x species. Those which were weakly adsorbed, desorbed as NH₃ between 200 and 300 °C, whereas those strongly adsorbed decomposed to yield H₂ and N₂ which was desorbed at 560 °C. Powder X-ray diffraction patterns of samples after denitridation were taken and presented in Fig. 6. In all cases, strong reflections corresponding to Mo metal can be observed. However, it is also apparent that both Au and Pd doped samples contain residual beta-phase nitride. This is consistent with the suppression of ammonia production upon hydrogenation observed with the dopants, although it should be noted that Au suppresses NH₃ formation the least and Pd suppresses it the most. The absence of intermediate phases with reduced nitrogen stoichiometry is consistent with our previous observations of denitridation of γ -Mo₂N [13] where denitridation leads to mixed phases of binary nitride and molybdenum metal. CHN analyses of the samples are presented in Table 3. It can be concluded that the majority of nitrogen which is lost is in the form of N₂. By comparison of the surface area data between Tables 2 and 3, it is apparent that surface area is lost upon denitridation, with the loss being greatest for the Ni doped sample. SEM investigation of the samples (Fig. 7) demonstrates that morphology is largely preserved upon nitrogen loss and that nitrogen elimination does not generate residual pores as observed in other nitride systems [32].

4. Conclusions

The addition of low levels of dopants has been shown to exhibit pronounced effects upon the morphology and nitrogen loss characteristics of beta-phase molybdenum nitride. Furthermore, the transformation pathways leading from molybdenum oxide precursors to the final nitride phase are affected. Au dopant appears to retard the formation of nitride, whereas Pd dramatically enhances it. In the case of Pd doped MoO₃, the formation of molybdenum bronze(s) occurs and these are proposed to be significant in terms of the observed enhanced surface area and

facilitated transformation of oxide precursor into nitride product. In general, the addition of dopants was observed to suppress the quantity of ammonia produced under temperature programmed reduction of nitrides and in the case of Pd and Au some retention of nitride phase was observed after reduction at 750 °C.

Acknowledgments

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