Freeze dried precursor-based synthesis of molybdenum bimetallic nitride

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Abstract

The molybdenum bimetallic nitride $MnMoN_2$ has been synthesized by ammonolysis of the stoichiometric amorphous precursor, obtained by freeze drying of aqueous solutions of the appropriate metal salts. The compound has been characterized by elemental analysis, energy-dispersive analysis of X-rays, X-ray diffraction, scanning electron microscopy, and thermogravimetry analysis under an oxygen atmosphere. $MnMoN_2$ crystallize in the hexagonal unit cell isostructural with β-$MnWN_2$ with a = 2.9226(6) Å, c = 10.8563(8) Å.. It is stable under oxygen atmosphere up to 250 °C, the oxidation of the bulk reverting to the $MnMoO_4$ oxide being complete at 530 °C.

Keywords: Freeze- dried precursor; Metallic nitride, Molybdenum, Manganese

1. Introduction

The investigation of transition metal nitrides is an emergent area in part due to the increasing number of applications of these materials [1]. Thus, in addition to traditional uses, based on mechanical properties [2], their chemical and structural versatility are leading to the discovery of new phases with exciting and important optical, electrical, magnetic and chemical properties [3–9]. Very few polymetallic nitrides have been synthesized and characterized, chiefly due to the limitations imposed by the preparation of these compounds. Only since the 1990s, with the development of new precursor synthesis methods has the systematic study of polymetallic nitrides been achievable.

Catalysis is a major driver in renewing interest in applied transition metal nitrides chemistry [10, 11]. The rapidly expanding studies of monometallic interstitial transition metal nitrides have demonstrated their potential to replace expensive noble group metal catalysts for important industrial processes [12]. One possible way of further improving their catalytic performance is to introduce other elements into the simple binary material. Molybdenum nitrides constitute examples of promising materials in this field due to their competitive activity and selectivity for commercially significant reactions including ammonia synthesis [13–15], hydrodenitrogenation and hydrodesulfurization [16–20].

Several synthetic approaches have been used towards preparing nitride catalysts. For example, first by the direct reaction of a metal nitride with other metals or nitrides; second by the reaction of a mechanical mixture of two metal powders with nitrogen or ammonia; third by the reaction between metal amides and nitrides; and fourth by the ammonolysis of mixed metallic oxides. A common feature of the newer synthesis methodol-ogies is the use of alternative reaction paths through which the cationic diffusion distances are reduced. This provides a route to obtain new nitrides at relatively low temperatures [25]. In this context, use of precursors obtained by freeze drying processing of the appropriate aqueous metal salts has proved to be a very versatile method for obtaining stoichiometrically controlled complex polymetallic systems [26–30]. It is well known that the preparative route plays a critical role in governing material properties, controlling the structure, morphology, grain size and surface area of the obtained materials.

Here we report how the use of novel freeze-dried polymetallic precursors has allowed us to synthesize the manganese-molybdenum nitride $MnMoN_2$.

2. Experimental

2.1. Synthesis

Materials used as reagents in the freeze drying method were ammonium molybdate $(NH_4)Mo_7O_{24}.4H_2O$ (Analar 99 %) and manganese(II) acetate $C_4H_6O_4Mn.\ 4H_2O$ (Janssen Chimica +99 %). Starting Mn or Mo solutions were prepared by dissolving their respective salts in distilled water. Then, they were combined to obtain $MnMoN_2$ source solution. Droplets of the resulting solution was flash frozen by projection on liquid nitrogen and then freeze-dried at a pressure of 1-10 Pa in a Heto Lyolab freeze-dryer. In this way, dried solid precursor was obtained as amorphous loose powder.

We attempted to prepare the transition metal nitride $MnMoN_2$ by ammonolysis of the adequate freeze dried precursor. The gases employed in the ammonolysis process were NH_3 and Ar. A sample of the selected precursor (0.2-0.3 g) was placed into an alumina boat, which was then inserted into an alumina tube furnace. The gas output of the tube furnace was connected to silicon oil trap and the input was connected to the gas line. Prior to initiating the thermal treatment, the tube furnace was purged for 10 minutes with Ar and another 5 minutes with NH_3. Several runs under different experimental conditions were also performed in order to determine the appropriate conditions for the preparation of pure samples.

2.2. Characterisation

2.2.1. Elemental analysis

Metal ratios in the solids were determined by energy-dispersive analysis of X-ray (EDAX) on a Jeol JSM 6300 scanning electron microscope. Data were collected with an Oxford detector, with quantification performed using virtual standards on the associated Link-Isis software. The operating voltage was 20 kV, and the energy range of the analysis 0–20 keV. The nitrogen content of the nitrides was evaluated by standard combustion analysis (EA 1108 CHNS-O); N_2 and CO were separated in a chromatographic column, and measured using a thermal conductivity detector. The oxygen content was determined by pyrolisis of a selected sample in an inert gas using a Carlo Erba_modelo 1500. Summarized in Table 1 are the results of these analyses for the resulting nitrides.

2.2.2. X-ray diffraction

X-ray powder diffraction patterns were obtained from a Phillips X'pert automated diffractometer using graphite-monochromated Cu-K_α radiation. Samples were dusted through a sieve on the holder surface. Patterns for phase identification were collected with a scanning step of 0.08° in 2θ over the angular range (2θ 10-80°) with a collection time of 5s per step. All graphical representations relating to X-ray powder diffraction patterns were performed using the WinPLOTR [31] program.

2.2.3. Microstructural characterization

The morphology of the precursors and the resulting nitrides was observed using a scanning electron microscope (Jeol JSM 6300) operating at an accelerating voltage of 30 kV. All the preparations were covered with a thin film of gold for better image definition.

2.2.4. Thermogravimetric analysis

The thermal stability of $MnMoN_2$ in air was determined by with a TG/DTA Perkin-Elmer instrument (Pyris Diamond) at a rate of 10K/min up to 900°C.

3. Results and discussion

Bimetallic manganese-molybdenum nitride was prepared from amorphous precursors, we have used Interstitial crystalline phases, which are tolerant to a certain non-stoichiometry range, have been characterized in each one of the individual Mo-N and Mn-N systems. The crystal structures of interstitial nitrides in most cases derive from an fcc or hcp arrangement of metal with N occupying octahedral sites in a more or less ordered way [32, 33]. Indeed, the respective compositions for the hexagonal interstitial crystalline phases have been characterized in these binary systems, with compositions δ-MoN [34] and ζ phases (Mn_5N_2 [35], Mn_2N [36,37] and $Mn_2N_{0.86}$ [38]). In addition, cubic nitride phases also have been given as γ-Mo_2N_{1+x} (-0,2 ≤x≤0,3) [34] and ε-Mn_4N [35, 39]. Other phases have been characterized, a low temperature phase (β-Mo_2N_{1+x}), [34] η-Mn_3N_2 [40] and θ-$Mn_6N_{5.26}$ [41], in which an ordering transition of the N atoms results in a tetragonal structure.

In previous publications in this specific field, we approached the study of the influence of the procedural variables for obtaining single phased monometallic nitrides and bimetallic oxynitrides containing transition metals of the groups 5 and 6. Our success in the preparation of different systems of nitrides was based on the use of freeze-drying procedure of aqueous solutions of the appropriate metal salts and of careful control of the experimental conditions.

In the present work, we have extended our synthetic approach to the synthesis of multimetallic interstitial molybdenum nitrides [42, 43]. Our goal was then to investigate the optimal conditions for obtaining pure $MoMnN_2$ hexagonal phase. The precursor powder was heated at 5 K min^{-1} to a final temperature that was held for a period of time under flowing ammonia (50 cm^3min^{-1}). Then, the solid was cooled down at different variable rates under the same atmosphere. The different cooling rates were obtained by either turning off the oven and leaving the sample inside (slow, ca.2 K min^{-1}) or by quenching at room temperature (fast, ca.50 K min^{-1}).

From the above, we selected a nitridation temperature of 800 °C and fast cooling rate, after 12 h of thermal treatment, as the conditions to be adopted for the preparation of black product whose X-ray diffraction patterns (Figure 1) consist of single phase. Under these conditions, all the significant shortening of the reaction time, with regard to our preliminary experiments, did not change the result; reaction times as short as 2 h also yield single phase product. The powder X-ray diffraction pattern was indexed to a hexagonal unit cell isostructural with β-$MnWN_2$ ($P6_3$/mmc) [44] with a = 2.9226(6) Å and c = 10.8563(8) Å.

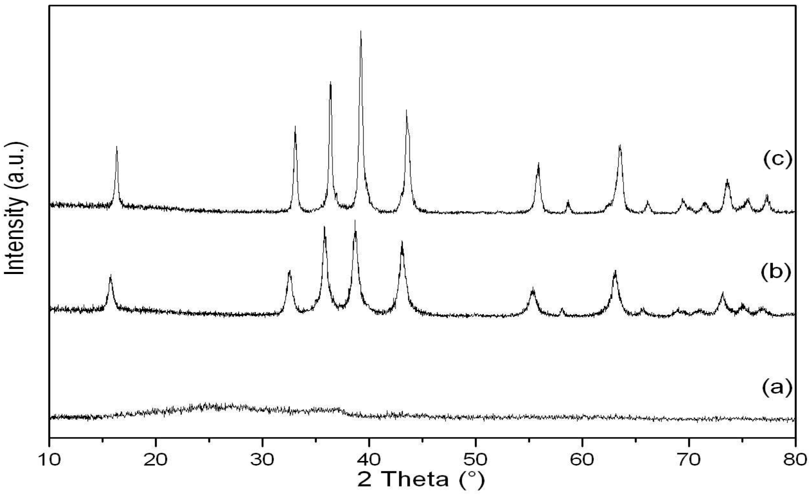

Figure 1 X-ray diffraction pattern of products resulted after ammonolysis of the freeze dried precursor under different temperatures. (a) freeze dried precursor, (b) T_f = 500 °C for 12h and (c) T_f = 700 °C for 12h.

Table 1 shows the results of metal analyses of the resulting product. In all cases, the Mn:Mo ratio is (within experimental error) equal to the nominal value in the corresponding precursor. In addition, the nitrogen is consistent with $MnMoN_2$ stoichiometry. Oxygen analysis did not detect any oxygen (<1) in the nitride samples, suggesting little or no oxygen uptake by the sample. Powder X-ray diffraction pattern of the sample exposed to the atmosphere for a period of one month did not change, confirming that the $MnMoN_2$ is stable to air and moisture.

According to the β-$MnWN_2$ phase, the atomic positions and bond distances are listed in Table 2. The Mo-N bond of 2.121 Å in $MnMoN_2$, similarly, is comparable to the Mo-N bond lenths of 2.095 and 2.091 Å found in $LiMoN_2$ [45] and the Mn-N distance of 2.213 Å is close to that found in β-$MnWN_2$, 2.118 Å. The structure of $MnMoN_2$ consists of layers of MnN_6 octaedra and MnN_6 trigonal prisms, the layers are staggered and stacked in the sequence AbAcBaBcA, were A and B represent the closed packed nitrogen atoms, c = manganese and a, b = molybdenum. Other nitrides that exhibit this structural motif with identical or similar stacking sequences include $LiMoN_2$ [45], β-$MnWN_2$ and Nb_5N_6 [44].

Table 1 Chemical composition, of manganese-molybdenum nitride $MnMoN_yO_z$

Sample	**Mn (EDAX)**	**Mo (EDAX)**	**Oxygen (wt %)**	**Nitrogen (wt %)**	**y**	**z**	**Proposed Stoichiometry**
1	1.02	0.97	< 1	15.2	1.91	< 0.1	$MnMoN_2$
2	0.98	0.99	< 1	16.1	2.04	< 0.1	
3	1.00	0.96	< 1	15.3	1.90	< 0.1	
medium	1.00	0.97	< 1	15.5	1.95	< 0.1	

Figure 2 shows the characteristic SEM images corresponding to the freeze-dried precursor and the final nitride. The ammonolysis reaction induces significant changes in the microstructure, affecting both the morphology and the particle size that the typical diameter around 500 nm. The size of the crystallite has been calculated from the XRD pattern by the standard Scherrer analysis of the half-width of the XRD peak [46]. Well crystallized LaB_6 was used as standard to calibrate the intrinsic width associated to the equipment. The average crystallite size was 42.5 nm.

Table 2 Crystal parameters and selected bond distances for $MnMoN_2$ (space group $P6_3/mmc$)

Atom/Wyckoff site	**x**	**y**	**z**
$MnMoN_2$ (a = 2.9226(6) Å, c = 10.8563(8) Å)			
Mn (2a)	0	0	0
Mo (2d)	1/3	2/3	3/4
N (4f)	1/3	2/3	0.1323(4)
Mn-Mn = 2.9224(6) Å; Mo-Mo = 2.9224(6) Å; Mn-Mo = 3.1958(2) Å, Mo-N = 2.121(1) Å; Mn-N = 2.213(2) Å; N-N = 2.564(7) Å			

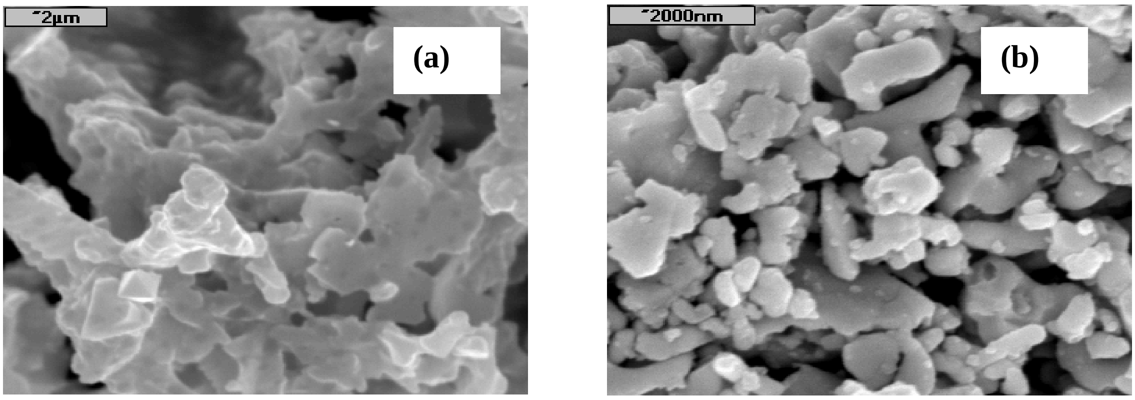

Figure 2 SEM images showing the microstructure of: (a) freeze-dried precursor and (b) the corresponding $MnMoN_2$ nitride.

TGA profile (figure 3) indicates that oxidation of the bulk sample of $MnMoN_2$ under an oxygen atmosphere begins at ca. 250 °C (under the conditions of the TGA experiments). This oxidation, which occurs in a one step process, is complete at ca. 530 °C, the final product was analysed by X-ray diffraction and being $MnMoO_4$ (figure 4).

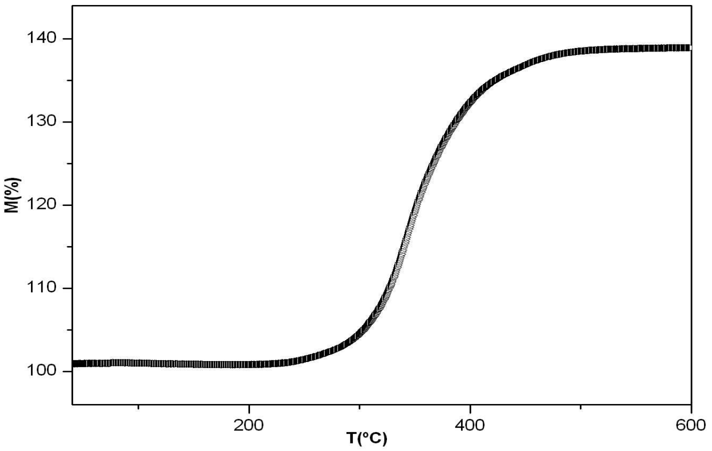

Figure 3 Characteristic TGA profile corresponding to $MnMoN_2$ nitride.

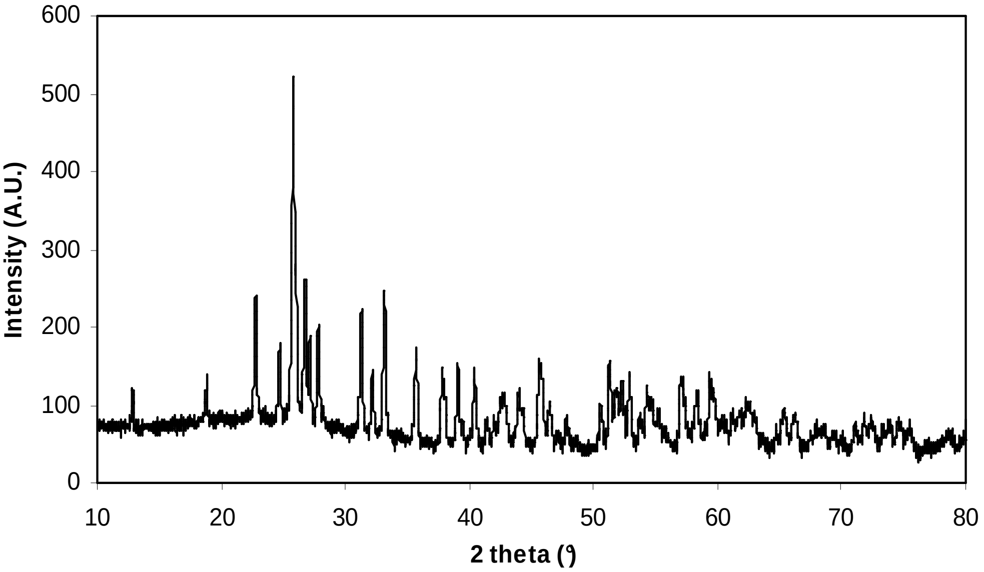

Figure 4 X-ray diffraction pattern of $MnMoO_4$ product resulted after oxidation of the bulk sample of $MnMoN_2$ under an oxygen atmosphere at 700 °C

4. Conclusion

Single phase $MnMoN_2$ have been prepared by ammonolysis of the corresponding freeze-dried precursor. It has been constated that freeze-dried precursor method is simple and that start with aqueous solutions, in the obtention of compounds with complex compositions, which can be alternative to the relatively long processes of amides and azide precursors.

On the other hand, the compounds are obtained as aggregates of nanometric spherical particles with typical diameter around 500 nm; this small particle size suggests high surface areas of materials. So, this method allows the obtention of samples with high surface area and with a careful tuning of the compositions, which are both key factors in homogeneous distribution of metals; preparation of catalysts, etc.

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