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Pd_2Mo_3N: a new molybdenum bimetallic interstitial nitride

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The molybdenum bimetallic nitride Pd_2Mo_3N has been synthesized by ammonolysis of the stoichiometric mixture of low sized pure oxide crystallites ($2PdO/3MoO_3$) as resulting from low temperature thermal decomposition of precursor powders obtained by freeze-drying of aqueous solutions of the appropriate metal salts. This compound has been characterized by elemental analysis, energy dispersive analysis of X-rays, X-ray diffraction, scanning electron microscopy (field emision) and thermogravimetry under oxygen atmosphere. Pd_2Mo_3N crystallizes in the cubic space group $P4_132$ (no. 213) (Pd_2Mo_3N, $a = 6.81770(3)$ Å, $Z = 4$), and presents the unusual filled β-manganese structure. It is stable under oxygen atmosphere up to 550 K, the oxidation of the bulk reverting to the oxide mixture being complete at 850 K.

Introduction

Research in the area of complex nitride chemistry is currently in full expansion because of the diversity of useful properties and emerging applications of these materials.[1] There is no doubt that such an accelerated progress in nitride chemistry beyond binary systems has been mainly based on the implementation of new preparation techniques in recent years.[2,3] A common feature of the new synthetic methodologies is their search for alternative reaction paths through which the cationic diffusion distances become lowered, which would enable nitride preparation at relatively low temperatures.[3,4] The use of bimetallic oxide precursors is the basis of one of these successful approaches.[5,6] This method has proved to be very useful when treating some well established compositions, but other methods must be used when the metal proportion in the final complex nitride differs from that of the starting oxide.[4,7] In this context, we have reported on the advantages of carrying out nitridation processes (under relatively mild conditions) of precursor powders resulting from freeze-drying of aqueous solutions containing metals in the required nominal stoichiometric ratio.[8,9] In practice, such a method has enabled us to prepare Ni_2Mo_3N,[4] together with a diversity of compositions in the solid solution series $V_{1-z}Mo_z(O_xN_y)$,[4,8] $V_{1-z}Cr_z(O_xN_y)$ and $Cr_{1-z}Mo_z(O_xN_y)$.[9]

Progress in nitride chemistry has allowed the identification of a set of favoured structure types, which have been carefully reviewed in refs. 2 and 3. In short, concerning bimetallic nitrides that contain only transition metals, the crystal structures of most of the known compounds can be classified as one of the following categories: (a) metallic antiperovskite structures, such as Fe_3NiN; (b) η-carbide-type structures, such as Co_3Mo_3N; and (c) layered structures, such as $CrWN_2$. Recently, after the structure determination of Ni_2Mo_3N[7,10] and Ni_2W_3N,[10] a new structural type came into existence in this sub-area of nitride chemistry – the filled β-Mn structure. In fact, the filled β-Mn structure has long been known for M_2T_3X carbide and nitride compositions including post-transition metals (M).[11] Prior to the description of Ni_2Mo_3N the existence of one β-Mn phase including two transition metals, Ni_2Cr_3N, was also observed, but no attempt to isolate and characterize it was made.

Besides their unusual properties, non-oxidic (carbides and nitrides) Mo- or W-containing materials have proved to be very efficient catalysts in different relevant processes,[1,12] including hydrodenitrogenation[6] and ammonia synthesis.[13] To expand possibilities, we have explored the opportunity of applying our synthetic methodology to the synthesis of new bimetallic Mo-containing nitrides. Here, we report on how the use of freeze-dried polymetallic precursors has allowed us, by adjusting the procedural variables to the peculiarities of palladium chemistry, to synthesize for the first time a new molybdenum bimetallic interstitial nitride, Pd_2Mo_3N, having the β-Mn structure.

Experimental

Synthesis

Materials used as reagents in the current investigation were $PdCl_2$ (Aldrich, 99.9%), NH_4Cl (Panreac, 99.5%) and $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ (Panreac, 99.0%). To avoid Pd hydrolysis, the starting Pd solution was prepared by dissolving $PdCl_2$ in an aqueous solution (0.1 M) of ammonium chloride. The Mo salt was then dissolved in this solution.

The total cationic concentration was 0.1 M, with the molar nominal composition for $Pd : Mo = 2 : 3$. The masses of the different reagents were adjusted to give 0.3 g of the final product. Droplets of this solution were flash frozen by projection on liquid nitrogen and then freeze-dried at a pressure of 1–10 Pa in a Telstar Cryodos freeze-drier. In this way, dried solid precursors were obtained as amorphous (X-ray diffraction) loose powders. A mixture of Pd and Mo crystalline oxides was obtained by heating the amorphous precursor for 12 h under oxygen at 723 K.

Both amorphous and crystalline precursors were used in ammonolysis experiments. The gases employed were NH_3 (99.9%) and N_2 (99.999%). A sample of the selected precursor (*ca.* 0.08 g) was placed in an alumina boat, which was then inserted into a quartz flow-through tube furnace. The back end of the tube furnace was connected to an acetic acid trap and the front end was connected to the gas line. Prior to initiating the thermal treatment, the tube furnace was purged for 30 min with N_2, and for a further 30 min with NH_3. Several runs under different experimental conditions were performed in order to determine the appropriate conditions for the preparation of pure samples. The precursor powder was heated at 5 K min^{-1} to a final temperature (T_f) that was held for a period of time

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(t_{hold}) under flowing ammonia (50 cm^3 min^{-1}). The solids obtained were then cooled at different variable rates (r_c) in 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}). After cooling, the products were purged with N_2 for 30 min.

Characterization

Elemental analysis. Metal ratios in the solids were determined by energy dispersive analysis of X-rays (EDAX) on a Jeol JSM 6300 scanning electron microscope, using an Oxford detector with quantification performed using virtual standards on 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 oxynitrides was evaluated by standard combustion analysis (Leco CHNS-932); N_2 and CO were separated on a chromatographic column, and measured using a thermal conductivity detector. The oxygen content was determined indirectly by thermogravimetric analysis (Perkin Elmer TGA 7 system).

X-Ray diffraction. X-Ray powder diffraction patterns were obtained from a Siemens D501 automated diffractometer using graphite-monochromated Cu-Kα radiation. Samples were dusted through a sieve on the holder surface. Routine patterns for phase identification were collected with a scanning step of 0.08° in 2θ over the angular range 20–90° 2θ with a collection time of 5 s per step. The refinement of the structures was performed using the FULLPROF program,[14] from patterns collected with a scanning step of 0.02° in 2θ, over a wider angular range (20–140° 2θ), and with a longer acquisition time (10 s per step) in order to enhance the statistics. All graphical representations concerning X-ray powder diffraction patterns were performed using the DRXWin program.[15]

Microstructural characterization. The morphology of both the crystalline precursors and the resulting nitrides was observed using a scanning electron microscope (Hitachi S-4100) operating at an accelerating voltage of 30 kV. All preparations were covered with a thin film of gold for better image definition.

Results and discussion

Synthesis and chemical characterization

Obtaining single-phase Ni_2Mo_3N under mild conditions starting from aqueous solutions of common metal salts was the goal of a previous work[4] whose conclusions were later extended to the synthesis of other related phases.[8,9] As indicated in the Experimental section [use of $NH_4Cl_{(aq)}$ as solvent], Pd chemistry requires some procedural modifications in order to obtain Pd_2Mo_3N. Thus, we carried out ammonolysis procedures using amorphous precursors under conditions similar to those reported as optimal in ref. 4. After preliminary results, both temperature and reaction times were varied over wide ranges (1073–1273 K, 2–48 h, slow *vs.* fast cooling). Regardless of the reaction conditions, the ammonolysis of the amorphous precursors resulted in black products whose X-ray diffraction patterns (Fig. 1a) do not correspond to a single phase. In fact, such patterns indicate that the ammonolysis products consist of a mixture of a majority phase, isostructural with Ni_2Mo_3N, with small quantities of molybdenum-containing phases (mainly Mo_2N). EDAX analyses gave average Pd : Mo ratios in the bulk samples lower (1.8 : 3) than the nominal one, this indicating that somewhere along the ammonolysis process some of the palladium was lost (in the form of some unidentified volatile product).

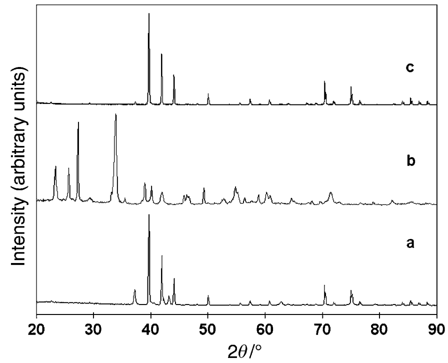

Fig. 1 X-Ray diffraction patterns of the products resulting after (a) ammonolysis of the amorphous precursor; (b) treatment in air of the amorphous precursor (crystalline precursor) and (c) ammonolysis of the crystalline precursor.

To avoid volatility losses, we subjected the amorphous precursors to thermal treatments at relatively low temperatures under an air atmosphere. After treatment at 723 K for 12 h the amorphous precursors were transformed into brown solids whose X-ray diffraction patterns (Fig. 1b) indicated that they were a mixture of PdO (JCPDS 41,1107) and MoO_3 (JCPDS 05,0508). These solids were used as crystalline precursors in the ammonolysis processes (once confirmed by EDAX analyses that the average Pd : Mo ratio in the bulk samples was, within the experimental error, the stoichiometric one of 2 : 3). It is evident that the low temperature formation of PdO under air atmosphere avoids palladium losses.

The ammonolysis of the crystalline precursor (2PdO : $3MoO_3$) at 1273 K for 10 h leads to a nearly single phase isostructural with Ni_2Mo_3N. In constrast to the Ni_2Mo_3N case,[4] this result does not depend upon the rate of the cooling process, which reflects the different chemical affinity towards nitrogen of Ni and Pd. Given the irrelevance of this parameter in this specific case, we adopted for simplicity and used a slow cooling rate in our preparative procedure. Under these conditions, the X-ray diffraction pattern of the product also displayed small peaks attributable to Pd metal (JCPDS 46-1043) and Mo_2N (JCPDS 25-1366). The intensities of the impurity peaks decreased as the thermal treatment time (at this temperature) was increased. After 6 days, the impurity peaks practically disappeared (Fig. 1c). EDAX analysis of this confirmed a homogeneous Pd : Mo = 2 : 3 composition, within experimental error, throughout the entire sample, and the nitrogen content (2.4%, combustion analysis) was consistent with the Pd_2Mo_3N stoichiometry. TGA experiments indicated that surface oxidation was irrelevant.

Structure refinement and description of the structure of Pd_2Mo_3N

The structure of the Pd_2Mo_3N phase was refined in the space group $P4_132$ from room temperature X-ray diffraction data. The starting structural model was that of Ni_2Mo_3N. In the structural refinement, the presence of impurities (Pd and Mo_2N) was also considered. The fits were performed using a pseudo-Voigt peak-shape function. In the final runs, usual profile parameters (scale factors, background coefficients, zero-points, half-width, pseudo-Voigt and asymmetry parameters for the peak-shape) and atomic positions were refined. Isotropic thermal parameters were set at 0.3 and 0.7 Å^2 for metals and nitrogen atoms, respectively, and an overall thermal parameter was also refined. The structural data are shown in Table 1. Fig. 2 shows the observed and calculated patterns. Residuals given in Table 1 are the conventional (background corrected) peak-only Rietveld profile and weighted profile residuals, R_p and R_{wp}, and the integrated intensity and structure factor residuals, R_B and R_F. A selected list of bond

Table 1 Structural data from X-ray powder diffraction studies of Pd_2Mo_3N[a]

Atom	Wyckoff position	*x*	*y*	*z*
Pd	8c	0.18890(11)	0.18890(11)	0.18890(11)
Mo	12d	0.79742(11)	0.04742(11)	1/8
N	4b	7/8	7/8	7/8

[a] Space group $P4_132$, $a = 6.81770(3)$ Å; $R_P = 12.8$, $R_{wp} = 14.1$, $R_B = 5.06$, $R_F = 4.92$.

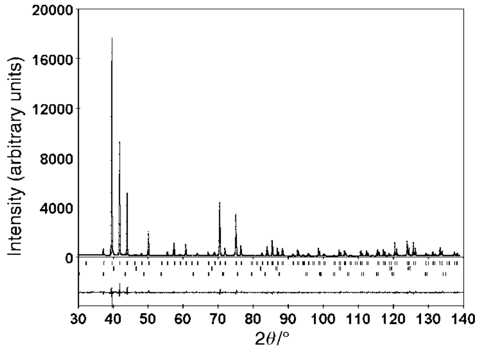

Fig. 2 Observed (dotted) and calculated (solid) X-ray diffraction profiles for Pd_2Mo_3N. Tic marks below the diffractograms represent the allowed Bragg reflections (top, Pd_2Mo_3N; center, Pd; bottom, Mo_2N). The residual line is located at the bottom of the figure.

distances is summarized in Table 2. It must be stressed that, for a better estimation of the accuracy of the parameters, the standard deviations (that relate only to the precision of parameters) must be multiplied by the SCOR parameter, according to ref. 16. The SCOR parameter has a value of 2.1769.

The structure of Pd_2Mo_3N consists of a β-Mn arrangement of metallic atoms (Pd and Mo), with N atoms occupying distorted octahedral interstitial sites. In the β-Mn structure (space group $P4_132$) there are two different types of metallic atom site which differ in their electronic states and are inherently predisposed to occupation by different atoms, due to their different multiplicities and bond distances.The result is that the Pd atoms are located in a 12-fold, pseudo-icosahedral coordination (Wyckoff position 8c), surrounded by three Pd and nine Mo atoms, giving $Pd[Pd_3Mo_9]$ units. In turn, the Mo atoms are located in a 14-fold (Wyckoff position 12d), pseudo-tetradecahedron site, surrounded by six Pd, six Mo and two N atoms, giving $Mo[Pd_6Mo_6N_2]$ entities. Finally, each N atom (Wyckoff position 4b) is surrounded by six Mo atoms, defining a distorted octahedron. These $[NMo_6]$ octahedra share corners. Fig. 3 shows the coordination polyhedra about each of the three different atoms in the Pd_2Mo_3N structure.

In short, the situation is identical to that in Ni_2Mo_3N, except for the differences concerning structural parameters related to the larger size of palladium atoms compared with nickel ones. In this sense, the discussion on bond distances as a function of the bonding nature in ternary nitrides held in ref. 7 maintains its significance (while incorporates new data).

Table 2 Selected bond distances (Å) for Pd_2Mo_3N

Pd–Pd ×3	2.5631(11)
Pd–Mo ×3	2.7555(10)
Pd–Mo ×3	2.8712(11)
Pd–Mo ×3	2.8912(10)
Mo–Mo ×4	2.8588(9)
Mo–Mo ×2	2.8794(11)
N–Mo ×6	2.1370(7)

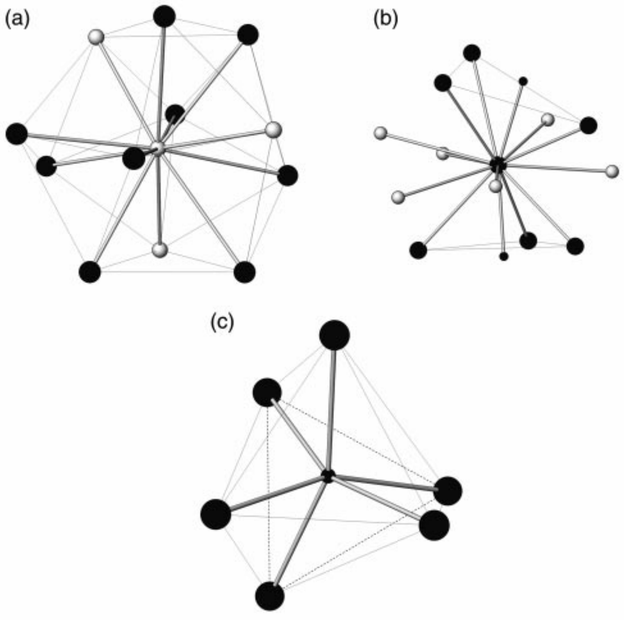

Fig. 3 The cubic symmetry of the β-Mn arrangement of metallic atoms is clearly shown in (a) $Pd[Pd_3Mo_9]$ pseudo-icosahedra and (b) $Mo[Pd_6Mo_6N_2]$ pseudo-tetradecahedra; nitrogen atoms occupy those distorted octahedral interstitial sites which are defined by only Mo atoms, (c) $[NMo_6]$.

Microstructural characterization and oxidation behavior

Fig. 4 shows characteristic SEM images corresponding to representative samples of both the crystalline precursor and the final nitride. As can be observed, the simultaneous low temperature *in situ* formation of PdO and MoO_3 results in a very intimate mixture of very low sized particles in which MoO_3 sheets appear to be surrounded by submicrometric PdO crystallites. The ammonolysis treatment induces significant changes in the microstructure, affecting both the particle size and morphology. These changes clearly indicate that the transformation during nitridation is not pseudomorphic, in contrast to that observed in the nitridation of pure molybdenum oxide.

As observed for other complex metal-rich interstitial nitrides such as Ni_2Mo_3N (β-Mn structure)[4,7] or M_3Mo_3N (η-carbide structure),[7] Pd_2Mo_3N is stable towards surface oxidation under air. This clearly contrasts with the observed behaviour in the case of rock-salt interstitial nitrides with comparatively high nitrogen to metal contents, such as $V_{1-z}Mo_z(O_xN_y)$,[4,8] $V_{1-z}Cr_z(O_xN_y)$ and $Cr_{1-z}Mo_z(O_xN_y)$[9] (a result which should have to be interpreted in terms of the significant observed morphological differences between both nitride types; rock-salt interstitial nitride grain growth as aggregates of nanosized crystallites showing such a high surface area as to make them pyrophoric). In fact, the oxidation of bulk samples of Pd_2Mo_3N under an oxygen atmosphere begins at *ca.* 550 K (under the conditions of the TGA experiments). This oxidation, which occurs in a two-step process, is complete at *ca.* 850 K, the final products being MoO_3 (JCPDS 05,0508) and PdO (JCPDS 41,1107).

In conclusion, we have prepared a new molybdenum bimetallic interstitial nitride, Pd_2Mo_3N. This compound is a new member in a singular structural family in the area of nitride chemistry, the β-Mn structure, which, to-date, only included Ni_2Mo_3N and Ni_2W_3N.

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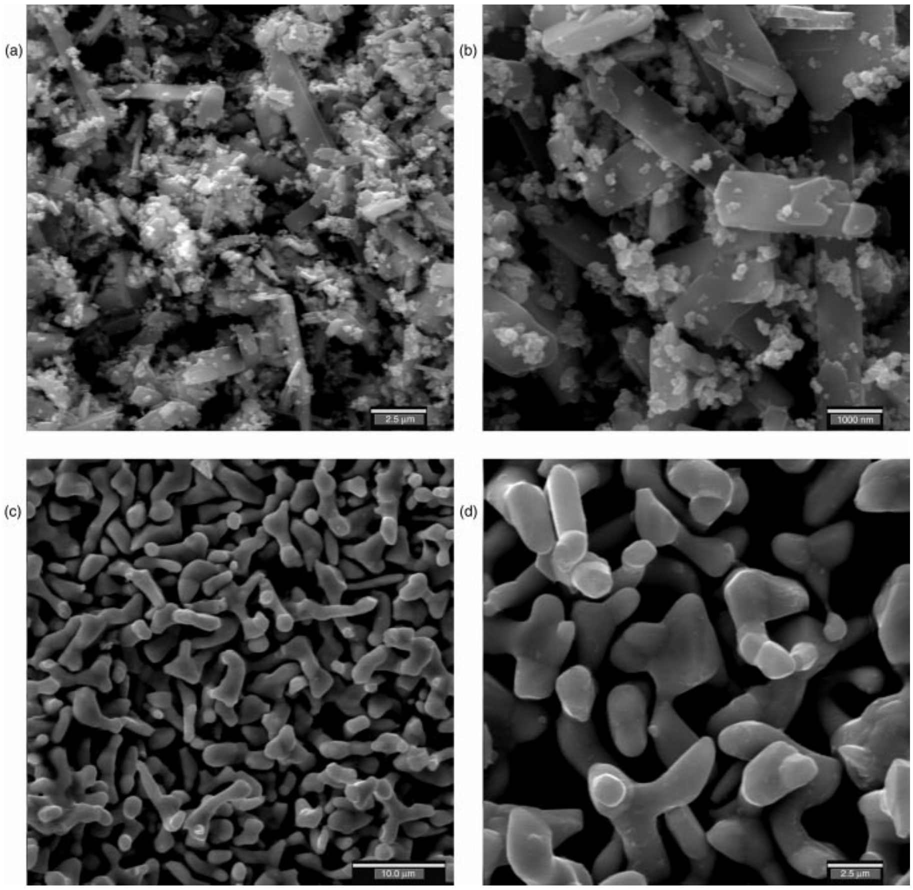

Fig. 4 SEM images showing the microstructure of the crystalline precursor (a and b) and the nitride (c and d). Scale bars correspond to 2.5, 1.0, 10.0 and 2.5 µm, respectively.

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