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Pt_2Mo_3N and $PdPtMo_3N$: new interstitial nitrides prepared from freeze-dried precursors

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Abstract

The molybdenum bimetallic and trimetallic nitrides Pt_2Mo_3N and $PdPtMo_3N$ have been synthesized by ammonolysis of the stoichiometric amorphous precursor, obtained by freeze drying of aqueous solutions of the appropriate metal salts. These compounds have been characterized by elemental analysis, energy-dispersive analysis of X-rays, X-ray diffraction, scanning electron microscopy, transmission electron microscopy and thermogravimetry analysis under an oxygen atmosphere. Pt_2Mo_3N and $PdPtMo_3N$ crystallize in the cubic space group $P4_132$ (213), with lattice parameters of $a = 6.83586(4)$ and $6.82542(3)$ Å, respectively, and form with the unusual filled β-manganese structure. These compounds are stable under air up to 580 K, the oxidation being complete at 910 K.

Keywords: Metallic nitrides; Freeze-dried precursor; Pt_2Mo_3N; $PdPtMo_3N$; Molybdenum; Platinum; Palladium

1. Introduction

The investigation of transition metal nitrides and carbides 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].

Progress in nitride chemistry has allowed the identification of a set of favored structure types. Recently, after the structure determination of Ni_2Mo_3N [21–23], Ni_2W_3N [23] and Pd_2Mo_3N [24], a new structural type came into existence in the area of nitride chemistry, the filled β-Mn structure.

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 methodologies is the use of alternative reaction paths through

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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 new β-manganese-type bimetallic and trimetallic interstitial nitrides, Pt_2Mo_3N and $PdPtMo_3N$.

2. Experimental

2.1. Synthesis

Materials used as reagents in the current investigation were ammonium heptamolybdate tetrahydrate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, (Aldrich, 99.98%), ammonium hexachloropalladate (IV), $(NH_4)_2[PdCl_6]$ and ammonium hexachloroplatinate (IV), $(NH_4)_2[PtCl_6]$. $(NH_4)_2[PtCl_6]$ and $(NH_4)_2[PdCl_6]$ were prepared following the method described elsewhere [31].

Starting Pt-, Pd- and Mo-containing solutions were prepared by dissolving their respective salts in distilled water. The aqueous solutions were combined to obtain Pt–Mo and Pd–Pt–Mo mixtures with nominal metal molar ratios of 2:3 and 1:1:3, respectively. Droplets of these solutions were flash frozen by projection on liquid nitrogen and then freeze-dried at a pressure of 1–10 Pa in a Heto Lyolab 3000 freeze-drier. In this way, dried solid precursors were obtained as amorphous loose powders (by powder X-ray diffraction). The procedure for the ammonolysis of the precursor powders has been described in a previous paper [32].

2.2. Characterization

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 nitride 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 thermal stability of Pt_2Mo_3N and $PtPdMo_3N$ in air was determined by thermogravimetric analysis with a TG/DTA Perkin-Elmer instrument (mod. Pyris Diamond) at a rate of 10 K/min up to 1173 K. The oxidation for both metal nitrides begins at 580 K and is complete at 930 K.

2.2.2. X-ray diffraction and transmission electron microscopy

X-ray powder diffraction patterns were obtained from a Philips X'Pert Pro automated diffractometer, equipped with a primary monochromator and an X'celerator detector. Routine 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 5 s per step. The cell parameters of the products were obtained by profile fitting of the pattern using the Le Bail's method [33] as implemented in the FULLPROF program [34], from patterns collected with a scanning step of 0.017° in 2θ, over a wider angular range (2θ 5–120°), and with a longer acquisition time (50 s per step) in order to enhance the statistics. The fits were performed using a pseudo-Voigt peak-shape function. In the final runs, the usual profile parameters (scale factors, background coefficients, zero-points, half-width, pseudo-Voigt and asymmetry parameters for the peak shape) were refined. All graphical representations relating to X-ray powder diffraction patterns were performed using the WinPLOTR [35] program.

Samples for transmission electron microscope (TEM) work were prepared by dispersion of fine-ground material onto a holey carbon film. Electron diffraction (SAED) patterns were obtained using a JEOL 2011 electron microscope, operating at an accelerating voltage of 200 kV.

2.2.3. Microstructural characterization

The morphology of the freeze-dried precursors and the resulting nitrides were 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.

3. Results and discussion

As mentioned in Section 1, we previously reported the existence of single-phase Pd_2Mo_3N [24]. Our success in the preparation of this nitride 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 new multimetallic interstitial molybdenum nitrides. Our goal was then to investigate the optimal conditions for obtaining pure Pt_2Mo_3N and $PdPtMo_3N$ cubic phases.

Thus, we carried out ammonolysis procedures using amorphous precursors under conditions similar to those reported as optimal in our previous work [24]. In preliminary experiments, both temperature and reaction times were varied over wide ranges (1073–1273 K, 2–24 h, slow vs. fast cooling). Regardless of the reaction conditions with these limits, the ammonolysis of the amorphous precursors resulted in black products. The patterns indicate that the ammonolysis products consist of quasi-single phases, isostructural with Ni_2Mo_3N and Pd_2Mo_3N.

For Pt_2Mo_3N, a minor impurity of platinum metal was consistently observed. By analogy to the synthesis of Pd_2Mo_3N, to avoid the appearance of the platinum phase, we subjected the amorphous Pt precursors to thermal treatments at relatively low temperatures in air. After treatment at 673 K for 12 h, the amorphous precursors were transformed into brown solids. X-ray diffraction revealed those to be a mixture of PtO and MoO_3. These solids were used as crystalline precursors in the ammonolysis processes.

The ammonolysis of the crystalline precursor ($2PtO : 3MoO_3$) at 1173 K for 12 h leads to an almost single-phase product isostructural with Ni_2Mo_3N and Pd_2Mo_3N. The X-ray diffraction pattern of the product displays also small peaks ascribed to Pt metal. From our experiments, we conclude that the Pt_2Mo_3N is formed from either amorphous or crystalline precursors and is independent of the cooling rate. For simplicity, direct ammonolysis of the amorphous precursor and a slow cooling rate were finally adopted in our preparative procedure. The new quaternary nitride $PdPtMo_3N$ could be prepared by analogy to Pt_2Mo_3N (amorphous freeze-dried precursor, $T_{\text{final}} = 1173$ K, $t_{\text{hold}} = 12$ h, slow cooling). Similarly, a small quantity of platinum metal was a common impurity. The contents of platinum impurities determined from XRD data, using the Fullprof program [34], were 1.8% and 2.3% for Pt_2Mo_3N and $PtPdMo_3N$, respectively.

The nitrogen content, 2.2% and 2.3%, determined by combustion analysis is consistent with the Pt_2Mo_3N (Calc. $N(\%) = 2.02$) and $PdPtMo_3N$ (Calc. $N(\%) = 2.32$) stoichiometry, respectively.

The structures of Pt_2Mo_3N and $PdPtMo_3N$ were refined in the space group $P4_132$ from room temperature powder X-ray diffraction data. The starting structural model was that of Ni_2Mo_3N. In the structural refinement, the presence of Pt metal impurities was also considered. The results of the Rietveld refinement and atomic parameter for Pt_2Mo_3N and $PdPtMo_3N$ are shown in Table 1. Fig. 1 shows the observed and calculated patterns of Pt_2Mo_3N.

The isostructurality of Pt_2Mo_3N and Pd_2Mo_3N and the results of the structure refinement of $PtPdMo_3N$ allow us an assumption that the latter is a part of the

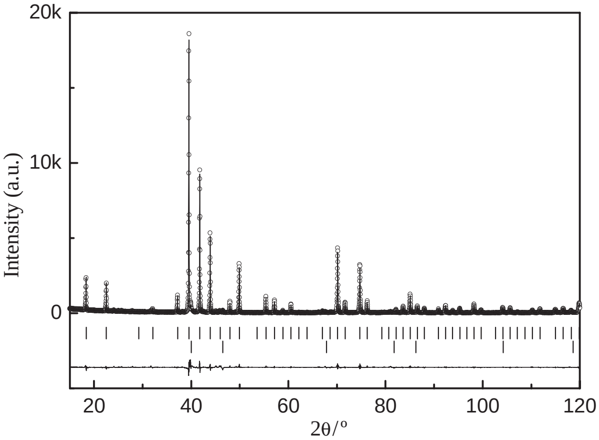

Fig. 1. XRD pattern of Pt_2Mo_3N showing observed (circles) and calculated (solid line) X-ray diffraction profiles for Pt_2Mo_3N. Tick marks below the diffractograms represent the allowed Bragg reflections (top, Pt_2Mo_3N; bottom, Pt).

Table 1
Crystal parameters and selected bond distances for Pt_2Mo_3N and $PtPdMo_3N$ (space group no. 213, $P4_132$)

Atom/Wyckoff site	*x*	*y*	*z*	B_{iso}
Pt_2Mo_3N ($a = 6.83586(3)$ Å)				
Pt (8*c*)	0.18759(11)	0.18759(11)	0.18759(11)	0.309
Mo (12*d*)	0.79773(17)	0.04573(17)	1/8	0.244
N (4*b*)	7/8	7/8	7/8	1.0
χ^2: 4.02; R_p: 9.96; R_{exp}: 3.78; $R_B = 5.94$; $R_F = 4.81$				
Pt–Pt = 2.5639(10) Å; Pt–Mo = 2.7655(13); 2.8808(9); 2.9044(14) Å; Mo–Mo = 2.8776(11); 2.8588(15) Å; Mo–N = 2.1392(7)				
$PtPdMo_3N$ ($a = 6.82542(3)$ Å)				
M (8*c*)[a]	0.19057(9)	0.19057(9)	0.19057(9)	0.389
Mo (12*d*)	0.79751(13)	0.04751(13)	1/8	0.210
N (4*b*)	7/8	7/8	7/8	1.0
χ^2: 5.34; R_p: 9.32; R_{exp}: 3.33; $R_B = 5.55$; $R_F = 4.33$				
M–M = 2.5738(9) Å; M–Mo = 2.7435(10); 2.8898(7); 2.8927(10) Å; Mo–Mo = 2.8614(13); 2.8842(12) Å; Mo–N = 2.1396(5)				

[a] M = Pt or Pd.

continuous solid solutions series between the ternary compounds.

All SAED experiments revealed the cubic crystal structure for Pt_2Mo_3N and no distortions or additional superstructure spots were observed. Selected area electron diffraction (SAED) patterns for Pt_2Mo_3N in the [010] and [$\bar{1}$20] zone axis are shown in Fig. 2. These SAED patterns were refined using the results obtained by XRD.

Since Pt_2Mo_3N and $PdPtMo_3N$ are isostructural, we will only discuss the structure of Pt_2Mo_3N, in detail. This structure consists of a β-Mn arrangement of metallic atoms (Pt 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 sites which differ in their electronic states and are inherently predisposed to occupation by different atoms, due to their different multiplicities. The result is that the Pt atoms are located in a 12-fold, pseudo icosahedral coordination (Wyckoff position 8*c*), surrounded by three Pt and nine Mo atoms, giving $Pt[Pt_3Mo_9]$ units. In turn, the Mo atoms are located in 14-fold (Wyckoff position 12*d*), pseudo tetradecahedron sites, surrounded by six Pt, six Mo and two N atoms, giving $Mo[Pt_6Mo_6N_2]$ entities. Finally, each N atom (Wyckoff position 4*b*) is octahedrally coordinated by molybdenum, forming a distorted octahedron. These $[NMo_6]$ octahedra share corners.

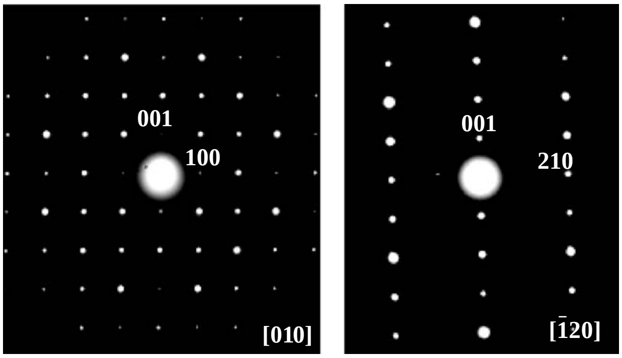

Fig. 2. Electron diffraction patterns of Pt_2Mo_3N in the zone axis [010] and [$\bar{1}$20]. The SAED patterns obtained have been indexed with the parameters found from X-ray diffraction.

Pd and Pt show metal radii quite close due to the well-known "lanthanide contraction", even they belong to different *d* element series, 4*d* and 5*d*, respectively. For this reason, the cubic *a* parameter changes only slightly from Pd_2Mo_3N ($a = 6.81770(3)$ Å [24]) to $PdPtMo_3N$ ($a = 6.82542(3)$ Å) and Pt_2Mo_3N ($a = 6.83586(3)$ Å), as metal radii also change slightly from Pd (1.370 Å) to Pt (1.385 Å) [36]. Consequently, there is no noticeable variation in both metal–metal and metal–ligand bond distances for Pd_2Mo_3N, $PdPtMo_3N$ and Pt_2Mo_3N (see Table 1).

Fig. 3 shows the characteristic SEM images corresponding to the freeze-dried precursors and the final nitrides. The ammonolysis reaction induces significant changes in the microstructure, affecting both the morphology and the particle size.

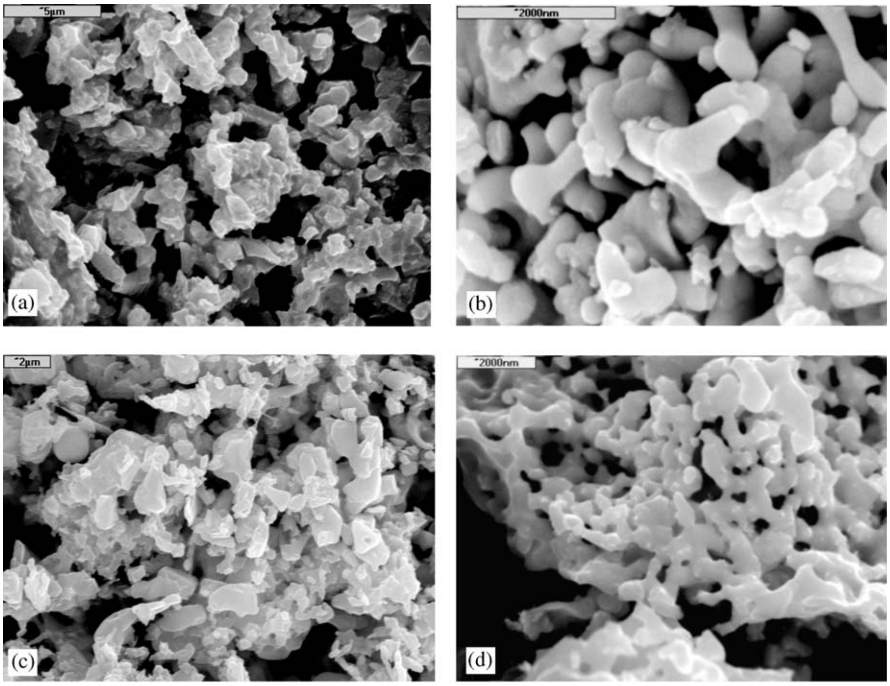

Fig. 3. SEM micrographs showing the microstructure of amorphous freeze-dried precursors of metal ratios Pt:Mo 2:3 (a) and Pd:Pt:Mo 1:1:3 (b), and the nitrides (c) Pt_2Mo_3N and $PdPtMo_3N$ (d).

In conclusion, we have prepared new molybdenum bimetallic and tetrametallic interstitial nitrides, Pt_2Mo_3N and $PdPtMo_3N$. These nitrides are new compounds in a singular β-Mn structural family in the nitride chemistry.

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