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Preparation of Transition Metal Nitrides using Unusual Routes

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Abstract

Two new methods are described to prepare transition metal nitrides. The first one is an original route using sulphides as nitridation precursors. As an illustration, heating MoS_2 and WS_2 under ammonia flow forms new molybdenum and tungsten nitride phases. The second method deals with the reaction of alkaline ternary oxides with ammonia which, in the case of the niobates ANb_3O_8 (A = Li, Na, K), gives access to $LiNb_3N_4$ and Nb_4N_5. © 1997 Elsevier Science Limited.

1 Introduction

Transition metal nitrides attract considerable attention in several application domains, especially in heterogeneous catalysis, when they present high specific surface areas. Except for γ-Mo_2N, W_2N and VN, the nitridation of an oxide (oxide + NH_3 $\rightarrow$ nitride + $H_2O\uparrow$) is generally unfavourable to produce high surface area powders; water vapour is generated during the reaction and can cause sintering. A new route to prepare nitrides has been developed using sulphides as starting products. The reaction has been applied first to the preparation of δ-MoN type nitride phases from MoS_2[1,2] and then extended to other transition metal elements: W, Cr and Ti.

On the other hand, alkaline and transition metal ternary oxides offer potentialities as nitridation precursors of transition metal nitrides. $LiMO_3$ and LiM_3O_8 vanadates, niobates and tantalates were recently reacted with ammonia giving rise to a series of new mixed-valence oxynitrides with cubic NaCl structure.[3,4] In this paper, we have pursued this study and shown that $LiNb_3O_8$ can lead to the ternary nitride $LiNb_3N_4$, whereas $NaNb_3O_8$ and KNb_3O_8 react to form the binary nitride Nb_4N_5.

2 Use of Sulphides as Nitridation Precursors

2.1 Preparation of high surface area precursors in molten salt medium

Previous works have shown the possibility to prepare MoS_2 in potassium thiocyanate melt from MoO_3 or Na_2MoO_4.[5] The experimental procedure consists in mixing intimately the starting product with a large excess of KSCN ($T_f = 177°C$). The mixture is placed in a quartz tube, slowly heated ($1°C\,min^{-1}$) up to 350°C in a muffle furnace. Na_2MoO_4 slowly dissolves at 200°C to give a yellow to red melt. At 350°C, a black precipitate is formed. MoO_3 is found to be more reactive since a black solid commences to precipitate as low as 200°C. The step temperature is maintained approximately during 15 h. After cooling, water soluble compounds are removed and the recovered powder is dried a few hours at 60°C then 110°C under vacuum. The main results of this study are indicated in Table 1. Under our conditions, only MoS_2 (JCPDS file 37-1492) precipitates and the reaction of MoO_3 appears to be more favourable to obtain high surface areas.[1,2] After adjustment of the reaction parameters, specific surface areas higher than $200\,m^2\,g^{-1}$ are usually obtained, which are useful in catalytic applications.[6] Chemical analysis of sulphur, performed in a LECO analyser, is in good agreement with the MoS_2 calculated value and the oxygen content is found lower than 2 wt%. The corresponding MoS_2 morphology is illustrated by the SEM micrograph of Fig. 1.

Following a similar process, WS_2 can be prepared from WO_3. However, the reaction must be carried out in NaSCN, rather than in KSCN, which melts at a higher temperature ($T_f = 287°C$). WS_2 (JCPDS file 08-0237) is prepared at 550°C with a specific surface area of $30\,m^2\,g^{-1}$. Under our operating conditions, no sulphide is obtained from chromium, titanium or niobium binary oxides either in KSCN or NaSCN melt, but Na_2CrO_4 reacts with KSCN to give $NaCrS_2$.

Table 1. Molten KSCN synthesis of MoS_2

Precursor	*Bath temperature (°C)*	*XRD analysis*	*Sg* (m^2g^{-1})
Na_2MoO_4	350	Poor crystalline MoS_2	10
MoO_3	300	Amorphous	190
MoO_3	350	Poor crystalline MoS_2	≥200

Table 2. Charaterizations of L-MoN and H-MoN

	750°C	*850°C*
Temperature increase (°C min^{-1})	15	15
NH_3 flow rate (l h^{-1})	35	35
Step time (h)	96	20
Oxygen content	0·85 wt%	0·6 wt%
Nitrogen content	15·0 wt%	13·1 wt%
Formulation	$Mo_{0{\cdot}82}N$ (L-MoN)	$Mo_{0{\cdot}96}N$ (H-MoN)
Density	7·4	8·1
Sg (m^2g^{-1})	16	7

2.2 Nitridation of sulphide precursors

The general reaction of ammonia with a sulphide can be written as follows, with H_2S gas formation:

$$MS_x \xrightarrow{NH_3} MN_y + xH_2S \uparrow$$

The study has been carried out with two starting materials, commercial sulphides with low surface area and higher surface area precursors prepared in molten thiocyanate medium.

2.2.1 Nitridation of MoS_2

2.2.1.1 Commercial MoS_2 Depending on the reaction conditions, two different nitrides, closely related to δ-MoN type are obtained (Table 2). L-MoN is prepared at lower temperature (750°C) than H-MoN (850°C).[1,2] Other nitridation parameters such as reaction time, ammonia flow rate and thickness of MoS_2 powder in the alumina boat must also be precisely controlled in order to avoid mixtures L-MoN + H-MoN at these temperatures. Neither of the two phases contains sulphur. The experimental formulations for L- and H-MoN are, respectively, close to Mo_5N_6 and MoN compositions (N wt% calc. for MoN: 12·74). Figure 2 displays the L-MoN and H-MoN XRD patterns. Comparison of the X-ray diffraction data with δ-MoN JCPDS file points out a similarity in the case of H-MoN except for the presence of a few extra weak peaks. In the case of L-MoN, the presence of other extra weak peaks is accompanied by a shift towards larger diffraction angles. The XRD patterns can be indexed in hexagonal unit cells (Table 3). There are close relationships with the δ-MoN unit cell described by Bezinge *et al.*[7] A neutron diffraction study is now in progress in order to determine the nitrogen atomic positions. The nitridation of commercial MoS_2 ($3\,m^2g^{-1}$) leads to an increase in the surface area; the lower the reaction temperature, the higher the surface area. BET surface area values are $16\,m^2g^{-1}$ and $7\,m^2g^{-1}$, for L-MoN and H-MoN, respectively. The two phases show superconducting properties at $T < 12K$.

Fig. 1. MoS_2 SEM micrograph (× 40 000).

2.2.1.2 High surface area MoS_2 precursor The results are summed up in Table 4. High surface

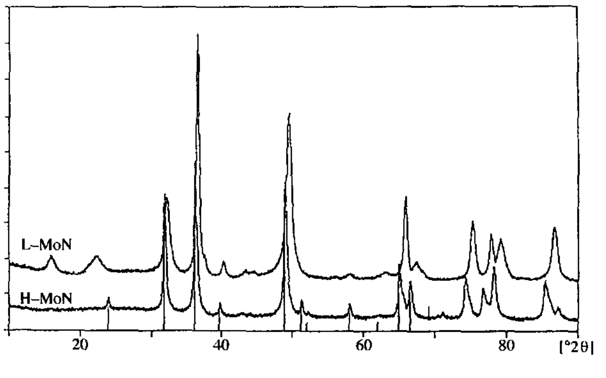

Fig. 2. L- and H-MoN XRD powder patterns compared with δ-MoN JCPDS file.

Table 3. Unit cell parameters comparison of δ-MoN, L-MoN and H-MoN

δ-MoN[7] ($P6_3mc$)	Mo_5N_6 (L-MoN)	MoN (H-MoN)
a = 5·745 Å	$d' \sim a\sqrt{3}/2 = 4{\cdot}893(1)$ Å	a″ = 5·733(2) Å
c = 5·622 Å	c′ ~ 2 c = 11·06(1) Å	c″ = 5·613(2) Å
V = 160·7 $Å^3$	$V' \sim 3/2\ V_{\delta\text{-MoN}}$	V″ = 159·8 $Å^3$

Table 4. Nitridation of high surface area MoS_2 at different temperatures

T (°C)		Sg (m^2g^{-1})
650	MoS_2 + L-MoN	140
690	L-MoN	50
750	L-MON + H-MoN	20
800	H-MON + L-MoN	10

Table 5. Nitridation of WS_2, Cr_2S_3 and TiS_2

Precursor	Molten salt	Bath temperature (°C)	XRD analysis	Nitridation temperature (°C)	XRD analysis	Sg (m^2g^{-1})
WO_3	NaSCN	550	WS_2 (30 $m^2 g^{-1}$)	800	$W_{0.83}N$	20
			WS_2 comm.	850	WS_2	—
			WS_2 comm.	875	$W_2N + W$	8
TiO_2	KSCN	350	TiO_2			
			TiS_2	600	TiN	90
			TiS_2	800	TiN	40
Cr_2O_3	KSCN	300	Cr_2O_3			
Na_2CrO_4	KSCN	350	$NaCrS_2$	800	CrN	—
			Cr_2S_3	700	CrN	15

area MoS_2 powders show an interesting reactivity with ammonia. Pure L-MoN is prepared with a relative high surface area. As seen before, formation of H-MoN occurs at higher temperatures. MoS_2 + L-MoN mixtures show high Sg values which range from 200 to 50 $m^2 g^{-1}$ depending on the proportion of nitride since the surface area of MoS_2 itself is not affected by the ammonia thermal treatment. Such values make the materials attractive for catalytic applications.

2.2.2 Nitridation of other sulphides

This method has been applied to the preparation of other transition metal nitrides. Table 5 indicates the main results obtained from tungsten, titanium and chromium sulphides.

Reaction between ammonia and commercial low surface area WS_2 (2 $m^2 g^{-1}$) occurs at $T > 850°C$, so that systematic presence of tungsten metal in the reaction products cannot be avoided whatever the ammonia flow rate. On the contrary, the sulphide issued from NaSCN melt (30 $m^2 g^{-1}$) reacts advantageously at lower temperature to give, at 800°C, a pure tungsten nitride hexagonal phase with parameters:

$$a = 5{\cdot}01\text{Å} \text{ and } c = 15{\cdot}26\text{Å}$$

At 900°C, another hexagonal phase is observed, accompanied by tungsten metal. This phase is closely related to the preceding one, as shown in Fig. 3:

$$d' = 2{\cdot}90\text{Å} \sim a/\sqrt{3} \text{ and } c' = 15{\cdot}30\text{Å} \sim c$$

Structural studies of these two phases are in progress.

Commercial TiS_2 and Cr_2S_3 powders react with ammonia thus forming TiN and CrN NaCl-type phases. When prepared at low temperature, the titanium nitride powders are characterized by high specific surface area up to 90 $m^2 g^{-1}$ (Table 5).

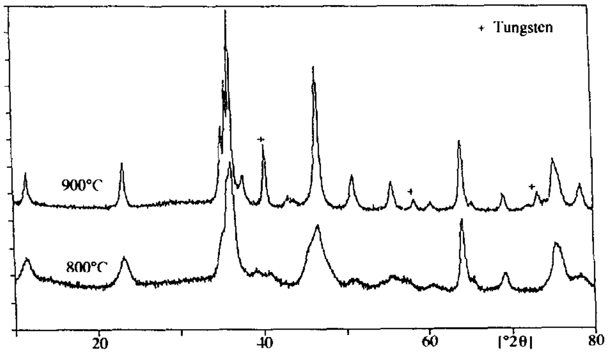

Fig. 3. XRD powder patterns corresponding to nitridation of WS_2 at 800 and 900°C.

Table 6. Chemical analysis of the $LiNb_3N_{4-\varepsilon}$ hexagonal phase

Sample	*(LECO method)*		*Experimental formulation $LiNb_3N_{4-\varepsilon}$*	*Density*	
	Oxygen (wt%)	*Nitrogen (wt%)*		*calc.*	*exp.*
1	0·5	15·5	$LiNb_3N_{3\cdot70}$	6·92	6·7
2	0·6	15·4	$LiNb_3N_{3\cdot71}$	6·93	6·6

Note lastly that nitrides can be directly elaborated in molten salt medium; such a preparation has been described elsewhere.[1,2] In particular, a new modification of Mo_2N molybdenum nitride resulting from the reaction $MoCl_5 + Ca_3N_2$ in molten calcium chloride has been identified as isostructural with rutile-type related α-Mo_2C.

3 Nitridation of Alkaline Niobates ANb_3O_8 (A = Li, Na, K)

3.1 $LiNb_3O_8$

$LiNb_3O_8$ is nitrided in flowing ammonia and leads to different reaction products depending on the temperature. At 800°C, a new cubic NaCl-type oxynitride phase is prepared with general formula $Li_{1\text{-}x}Nb_{3\text{-}3x}\square_{4x}(O,N)_{4\text{-}y}\square_y$ characterized by systematic presence of cationic and anionic vacancies in the unit cell.[3,4] The cubic parameter **a**, refined for $Li_{0\cdot74}N_{2\cdot22}\square_{1\cdot04}O_{0\cdot24}N_{2\cdot79}\square_{0\cdot97}$ composition, is equal to 4·326(1) Å corresponding to a random distribution in both subnetworks. At 1000°C, a purely nitrided phase is produced of composition close to $LiNb_3N_4$, i.e. without any evaporation of lithium. Oxygen and nitrogen chemical analysis results, given in Table 6, show very low oxygen content and a slight nitrogen deficiency with respect to $LiNb_3N_4$ formula. Figure 4 displays the X-ray powder pattern of this ternary nitride which is indexed with hexagonal parameters indicated in Table 7. $LiNb_3N_{4-\varepsilon}$ is isostructural with the ternary phase $Li_{1-x}Ta_{3+x}N_4$[8] and with the binary nitride Ta_5N_6.[9] The structural arrangement is of a filled up 2H-MoS_2 type consisting of alternate layers formed, respectively, with nitrogen prisms and octahedra.[6]

3.2 $NaNb_3O_8$ and KNb_3O_8

Reactive $NaNb_3O_8$ powder can be prepared by using the ion-exchange properties of KNb_3O_8.[10,11] This soft chemistry route consists in introducing KNb_3O_8 in a nitric solution (7N). A total exchange of potassium ions by hydronium ions leads to HNb_3O_8,H_2O and subsequent addition of sodium hydroxide solution forms the hydrate $NaNb_3O_8$, 2·5H_2O. Finally, $NaNb_3O_8$ is isolated after drying at 130°C.

Heated under ammonia flow, $NaNb_3O_8$ and KNb_3O_8, whatever their preparation method, behave identically, but different from $LiNb_3O_8$. At a temperature as low as 600°C, X-ray diffraction indicates formation of a mixture containing the ternary oxide $ANbO_3$ (A = Na or K) and a NaCl-type oxynitride phase Nb(O,N) (a = 4·31 Å). Consequently, the nitridation reactions have been pursued at a higher temperature by using directly $NaNbO_3$ and $KNbO_3$ as starting compounds. Contrary to the lithium niobate, both react in flowing ammonia with total evaporation of sodium or potassium, thus leading to the same result: at 800°C, the pure binary nitride Nb_4N_5 is prepared as shown by chemical analysis results reported in Table 8. From the XRD powder pattern, displayed on Fig. 5, a tetragonal unit cell is deduced with parameters indicated in Table 9. Nb_4N_5 is isostructural with Ta_4N_5[9,12] and Ti_4O_5.[13] The structure of Nb_4N_5 is built up from corner- and edge-sharing NbN_6 octahedra.[6] Superconducting properties occur at T < 10 K.

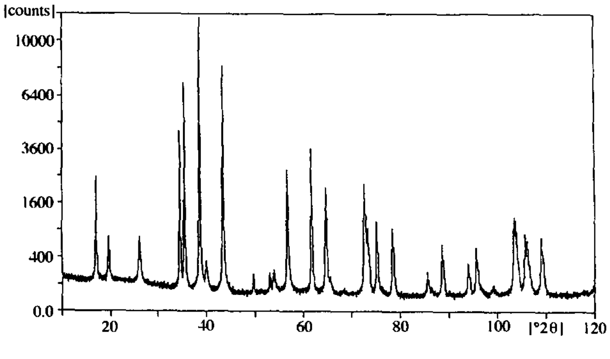

Fig. 4. XRD powder pattern of $LiNb_3N_{4-\varepsilon}$.

Table 7. $LiNb_3N_4$ structure data

	$LiNb_3N_4$	
	Space group: $P6_3mcm$	
	a = 5·2023(4) Å	*Z = 3*
	c = 10·362(1) Å	*V = 242·9 Å³*
	c/a = 1·99	
Atomic positions:	2 Li	2(b)
	1 Li + 3 Nb	4(d)
	6 Nb	6(g)
	12 N	12(k)

Table 8. Chemical analysis of Nb_4N_5

Sample	*(LECO method)*		*Formulation* NbN_x	*Density*	
	Oxygen (wt%)	*Nitrogen (wt%)*		*obs.*	*calc.*
1	0·7	15·85	$NbN_{1{\cdot}25}$	6·7	7·32
2	0·8	15·85	$NbN_{1{\cdot}25}$	6·7	7·32
3	0·85	15·8	$NbN_{1{\cdot}24}$	—	—
Calculated for Nb_4N_5:		15·86			

Table 9. Nb_4N_5 structure data

Nb_4N_5		
Space group: I4 m		
a = 6·853(1) Å *c = 4·270(2) Å*	*Z = 2* *V = 200·5 Å³*	
Atomic positions:	Nb	8(h)
	N	8(h)
	N	2(b)

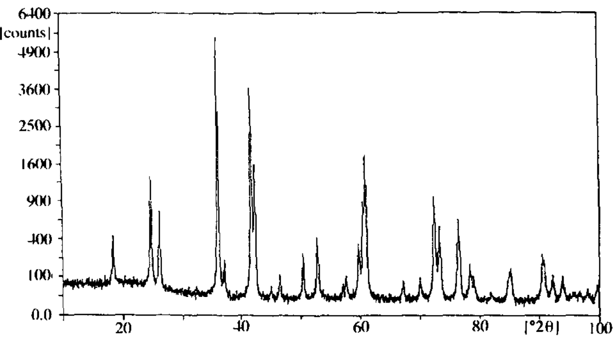

Fig. 5. XRD powder pattern of Nb_4N_5.

4 Conclusion

Among the methods presented here, nitridation of sulphide precursors is an original way to produce transition metal nitrides. New molybdenum and tungsten nitrides have been obtained by reaction of MoS_2 and WS_2 in flowing ammonia. This process can be applied to other starting products such as chromium or titanium sulphides. Preparation of high specific surface area precursors in thiocyanate melt proves to be attractive in the sense that they influence the nitride formation and properties.

This study has shown the possibility to prepare nitride compounds from alkaline niobates ANb_3O_8 with A = Li, Na and K. Under our conditions, only $LiNb_3O_8$ gives rise to the formation of a ternary nitride $LiNb_3N_4$. On the other hand, the reaction of $NaNb_3O_8$ and KNb_3O_8 with ammonia constitutes a new route to isolate, for the first time, bulk Nb_4N_5.

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