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An original way to prepare nitride-type compounds from sulfide precursors

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Abstract

Ammonolysis of transition metal sulfides contributes to the development of new preparation methods in nitride chemistry. In this work, the thermal reaction of MoS_2 in flowing ammonia has been extended to other transition metals such as tungsten, chromium and titanium. A new tungsten nitride W_5N_6 has been isolated as well as CrN- and TiN-related phases from the sulfides WS_2, Cr_2S_3 and $NaCrS_2$, and TiS_2, respectively. Either commercial products or reactive powders elaborated in thiocyanate melt were taken as precursors. © 1997 Elsevier Science S.A.

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1. Introduction

Reaction between ammonia and a sulfide, as a new possibility to prepare nitrides, was first reported in two recent papers devoted to new routes to molybdenum nitrides and oxynitrides [1,2]. Commercial MoS_2 powder reacts when heated in flowing ammonia to give at 750°C the new nitride composition Mo_5N_6 and at 850°C the δ-MoN phase [3,4]. X-ray and neutron diffraction studies have shown that the crystal structure of Mo_5N_6 is related to that of the precursor as it can be described as a filled up MoS_2-type structure. The nitrogen atoms form an AABB arrangement similar to the sulfur atom arrangement in MoS_2, in which the prismatic sites and 2/3 of octahedral sites are occupied by molybdenum atoms. δ-MoN is similar to the phase obtained by Bezinge et al. [5] under severe temperature and pressure conditions. Its crystal structure determination evidences both formation of triangular clusters of molybdenum and an ordered arrangement of nitrogen atoms.

On the other hand, in a context of catalytic applications, synthesis of MoS_2 powder with a high specific surface area ($S_g \geq 200$ m^2 g^{-1}) was performed in molten KSCN [2]. Such a reactive powder is transformed into the above nitrides at lower temperature, leading, for example, at $T < 700$°C to pure Mo_5N_6 with a surface area as high as 50 m^2 g^{-1} [3].

Owing to the interest of transition metal nitrides in many applications, we extend in the present study to other transition elements this new process to make nitrides from sulfide precursors, according to the general reaction:

$$MS_x + 2x/3NH_3 \rightarrow MN_y + xH_2S\uparrow + (x/3 - y/2)N_2\uparrow$$

in which H_2S gas is released, instead of water vapor in the classic preparation method involving an oxide as a starting product. In particular, tungsten, chromium and titanium nitride phases have been prepared and characterized from either a commercial

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sulfide or a sulfide precursor obtained from a molten salt medium.

2. Experimental

2.1. Synthesis

2.1.1. Precursor preparation

Among the sulfide precursors used in this study, WS_2 and $NaCrS_2$ have been elaborated in thiocyanate melt [3,4], WS_2 by reacting WO_3 at 550°C in molten NaSCN ($T_f = 287°C$) and $NaCrS_2$ by reacting Na_2CrO_4 at 350°C in molten KSCN ($T_f = 177°C$). The experimental procedure consisted of placing an intimate mixture of $WO_3(Na_2CrO_4)$ plus a large excess of thiocyanate, in a muffle furnace, and slowly heating it up (1°C min^{-1}) to the desired temperature which was maintained for ~ 15 h. After cooling, water-soluble compounds were removed and the recovered powder was dried for a few hours at 60°C, then 110°C, under vacuum. The other starting products, Cr_2S_3, TiS_2, but also WS_2, were supplied as commercial products.

2.1.2. Nitridation reactions

Nitridation reactions were carried out in an alumina boat placed inside an alumina tube through which ammonia gas flowed generally at a rate of ~ 20 l h^{-1} at 600°C and ~ 40 l h^{-1} at 900°C. The temperature was raised in the range 600–900°C, depending on the starting sulfide, with a heating rate of 5°C min^{-1}. The samples were held at their respective temperatures for ~ 2 days. The furnace was then switched off and the powder was allowed to cool to room temperature under nitrogen atmosphere. The release of H_2S is easily shown with a lead acetate paper.

2.2. Characterizations

2.2.1. X-ray diffraction analysis

XRD powder patterns were taken using a Philips (PW3710) diffractometer operating with CuKα radiation. PC-APD and PC-Identify Philips software were used respectively for recording, analysis and phase matching of the patterns.

2.2.2. Elemental analysis

A LECO analyzer provided simultaneously the nitrogen and the oxygen contents. The nitrogen and oxygen amounts are respectively measured as N_2 by thermal conductivity and as CO_2 by infrared detection. Sulfur was analyzed as SO_2 by IR at the Service Central d'Analyses du CNRS in Vernaison, France, where analysis of the nitrided phases showed systematic absence of sulfur.

2.2.3. Specific surface area determination

A Flowsorb II 2300 — Micromeritics apparatus was used to determine the specific surface area of the powders by the single point BET method. Before measurement, the samples were outgassed between 100 and 200°C for 30 min under He/N_2 gas flow.

3. Results

The different results we have obtained are discussed below and gathered respectively for each of the following transition elements studied: tungsten, chromium and titanium.

3.1. Tungsten sulfide

As in the case of molybdenum sulfide reported elsewhere [1–4], the ammonolysis of WS_2 was studied first with a commercial product of low specific surface area ($S_g = 2$ m^2 g^{-1}) and then with a high specific surface area sulfide powder ($S_g = 30$ m^2 g^{-1}) prepared in NaSCN melt.

3.1.1. Ammonolysis of commercial WS_2

Table 1 shows the reaction products at different temperatures when commercial WS_2 is heated under ammonia flow using either a low NH_3 flow rate (10 l h^{-1}) or a high NH_3 flow rate (30–50 l h^{-1} from 800 to 900°C). Whatever the flow rate, it can be pointed out that WS_2 reacts with NH_3 at much higher temperature than an equivalent commercial MoS_2 powder (see above). Under low NH_3 flow rate, the first nitrided phase to be formed, at ~ 850°C, is the nitride β-W_2N, which is accompanied at higher temperatures by increasing amounts of tungsten metal. However,

Table 1
Influence of the NH_3 flow rate on the nitridation of commercial WS_2 at different temperatures

Reaction temperature (°C)	NH_3 flow rate (l h^{-1})	Reaction time (h)	XRD analysis
800	< 10	60	WS_2
850	< 10	48	WS_2 + ε β-W_2N
875	< 10	48	β-W_2N + W
950	< 10	48	W + β-W_2N
800	30	48	WS_2
875	40	64	WS_2 + new nitride phase
900	50	21	WS_2 + new nitride phase + W
900	50	47	W + new nitride phase

Table 2
Chemical composition and specific surface area of tungsten nitride powders prepared in the 750–850°C temperature range

Temperature (°C)	Gas flow rate ($l\ h^{-1}$)	Reaction time (h)	Chemical analysis (wt.%)		Formulation (W_xN)	S_g ($m^2\ g^{-1}$)
			O	N		
750	30	72	1.6_5	8.3	$W_{0.84}N$	23
800	30	72	1.3_5	8.5	$W_{0.82}N$	19
850	40	67	0.9	8.3	$W_{0.84}N$	16

under high NH_3 flow rate, β-W_2N does not appear, but the new nitride phase which is detected in the XRD powder patterns is always accompanied either by unreacted WS_2 or by tungsten metal, depending on the temperature.

3.1.2. Ammonolysis of high surface area WS_2 powder

The reactivity in the solid-gas nitridation reaction is clearly improved when starting from a sulfide powder with a high specific surface area ($S_g = 30\ m^2\ g^{-1}$) prepared in NaSCN melt. Under these conditions, it is possible to prepare the above-mentioned new nitride phase in a pure state. The X-ray diffractograms of Fig. 1 show that it forms at a temperature as low as 750°C. Table 2 shows the elemental analysis results of nitrogen and oxygen, and corresponding specific surface area values, for different preparation temperatures ranging from 750–850°C. The very low oxygen content measured in the samples reveals that a nitride has been isolated, with the composition W_5N_6 ($W_{0.83}N$). The surface area of this new tungsten nitride decreases with temperature and at the same time its crystallinity increases, as displayed in Fig. 1. Though lower compared to the starting material, relatively high values of surface area are kept after nitridation in spite of the high temperature treatment.

W_5N_6 decomposes at ~900°C with formation of another tungsten nitride phase and tungsten metal. Fig. 2 compares the XRD powder patterns of two reaction products resulting from nitridation at 800°C (W_5N_6) and at 900°C (high temperature nitride phase + W). Except for the presence of tungsten metal and a better crystallization state of the high temperature phase, they are quite similar and only differ in the presence (or absence) of a few weak peaks. They can be indexed with the following unit cell parameters:

W_5N_6:	hexagonal	$a = 5.014(8)$ Å	$c = 15.26(3)$ Å
H.T. phase:	hexagonal	$a' = 2.9016(8)$ Å	$c' = 15.294(8)$ Å

The second set of parameters is related to the first one by:

$$a = a'\sqrt{3} \quad c \approx c'$$

Moreover, the parameters a' and c' are very close to those determined by Khitrova and Pinsker [6,7] for

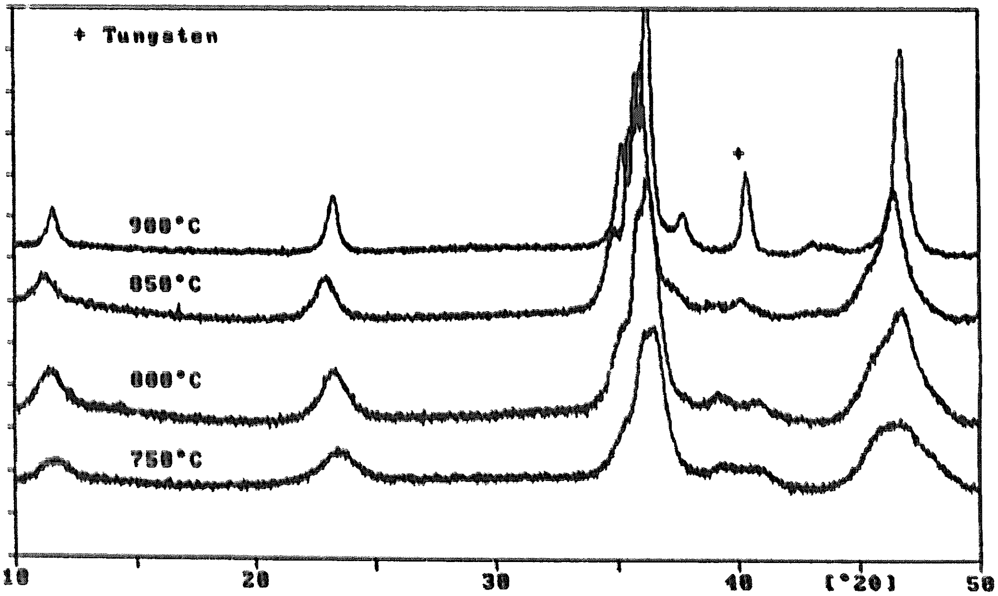

Fig. 1. XRD patterns of tungsten nitride powders prepared from 750 to 900°C.

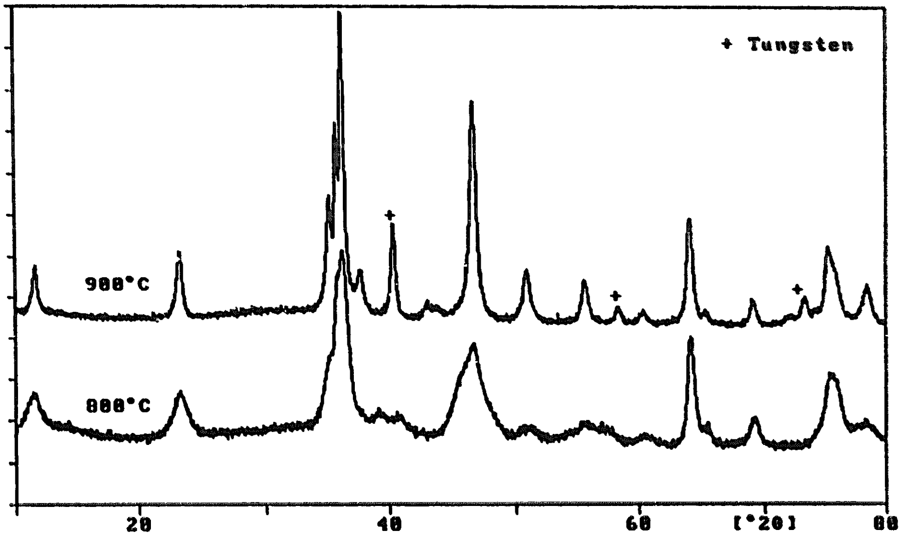

Fig. 2. Comparison between tungsten nitride diffractograms obtained after reaction at 800 and 900°C.

a tungsten nitride of composition $W_{4.6}N_4$, prepared as a thin film. This nitride has a layered crystal structure with a partially vacant metal atom arrangement where nitrogen atoms occupy only trigonal prismatic sites [6,7]. The corresponding calculated X-ray diffractogram matches very well the experimental XRD powder pattern of the H.T. tungsten nitride phase prepared in this work as a bulk material, so that similarity is assumed in the crystal structure and chemical composition. The structure of W_5N_6, which is different from Mo_5N_6, is also closely related.

3.2. Chromium sulfide

In order to prepare a reactive chromium sulfide powder, different oxide precursors have been tested in thiocyanate medium, such as Cr_2O_3, CrO_3, $K_2Cr_2O_7$ or Na_2CrO_4. Under the conditions used, only Na_2CrO_4 reacted with KSCN to give rise to the thiochromite $NaCrS_2$ (20 m^2 g^{-1}) [3,4]. A subsequent ammonolysis at 800°C of this ternary sulfide resulted in a total sodium evaporation and in the formation of stoichiometric binary chromium nitride CrN.

In Table 3 results of the direct nitridation of commercial binary sulfide Cr_2S_3 are gathered. It reacts in flowing non-purified commercial ammonia at a temperature as low as 600°C. Under these conditions, an oxynitride Cr(O,N) phase with a rock salt-type structure is formed. The oxygen content (~5 wt.%) progressively decreases as the nitridation temperature increases. It is very low at 700°C and negligible at 800°C when the nitrogen content of the reaction product reaches the value calculated for CrN (N wt.% = 21.22). Fig. 3 compares XRD powder patterns made after reaction at 600 and 800°C. They evidence a slight shift in the peak positions corresponding to a small decrease in the cubic unit cell parameter value when the temperature increases. The better crystallization state observed at high temperature results in a lower specific surface area whose maximum value is found in the experiment carried out at 700°C. Let us note that another process has been recently developed in our group to prepare highly dispersed chromium oxynitride powders with specific surface areas higher than 100 m^2 g^{-1} [8]. It consists actually in nitriding reactive chromium hydroxide powders at temperatures lower than 700°C.

3.3. Titanium sulfide

The oxophilic character of early transition metals explains here again that no reaction occurred from

Table 3
Characteristics of chromium (oxy)nitride powders prepared in the 600–800°C temperature range

Temperature (°C)	Chemical analysis (wt.%)		Experimental formulations		Lattice parameter (Å)	S_g (m^2 g^{-1})
	O	N	CrO_xN_y	CrN_z		
600	4.9	18.1	$CrO_{0.21}N_{0.87}$	–	4.146(1)	7
650	–	–	–	–	4.145(1)	10
700	2.5	20.0	$CrO_{0.11}N_{0.96}$	$CrN_{0.93}$	4.142(1)	15
800	1.4	21.15	–	$CrN_{0.99}$	4.141(1)	5

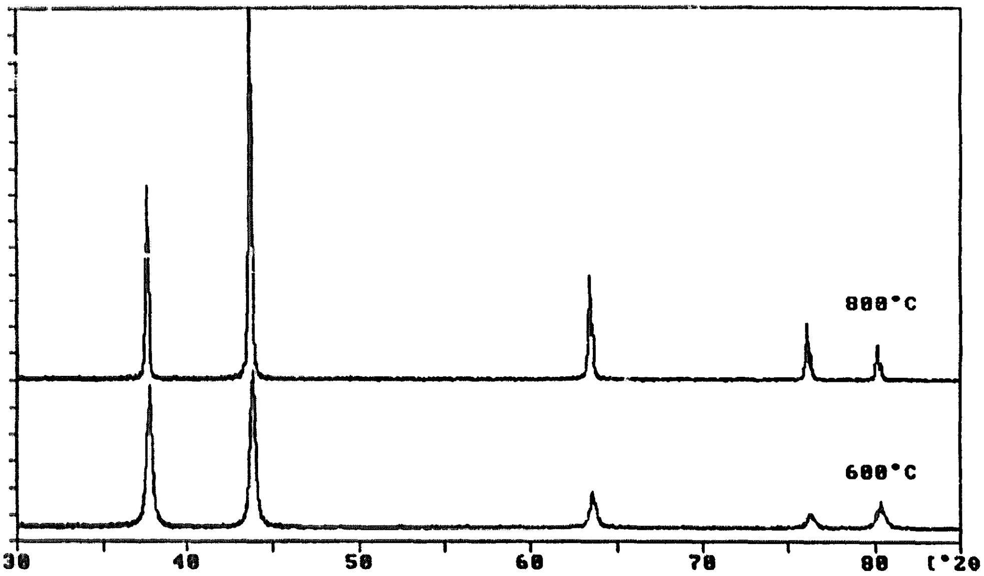

Fig. 3. XRD patterns of chromium (oxy)nitride powders prepared at 600 and 800°C.

TiO_2 when introduced in KSCN or NaSCN melt. Consequently, a commercial product was used as a precursor. This TiS_2 powder, sensitive to hydrolysis, contained impurities mainly identified as free sulfur.

Titanium sulfide reacts in flowing non-purified commercial ammonia to form a series of black cubic oxynitride phases, closely related to the NaCl-type nitride TiN which is characterized by a gold yellow

Table 4
Characteristics of titanium oxynitride phases prepared at 600–800°C

Temperature (°C)	Chemical analysis (wt.%)		Experimental formulation	d_{OX} Ti	Lattice parameter (Å)	S_g ($m^2\ g^{-1}$)
	O	N	TiO_xN_y			
600	13.6	16.9_5	$TiO_{0.69}N_{0.83}$	3.9	4.189(1)	85
650	12.5	19.2_5	$TiO_{0.55}N_{0.96}$	3.9	4.192(1)	60
700	7.8	21.0_5	$TiO_{0.33}N_{1.01}$	3.7	4.209(1)	50
800	6.1	21.1	$TiO_{0.25}N_{0.99}$	3.5	4.215(1)	37
900	3.1	22.9	$TiO_{0.13}N_{1.06}$	3.4	4.221(1)	—

TiN: $a = 4.2417$ Å; N wt.% = 22.63.

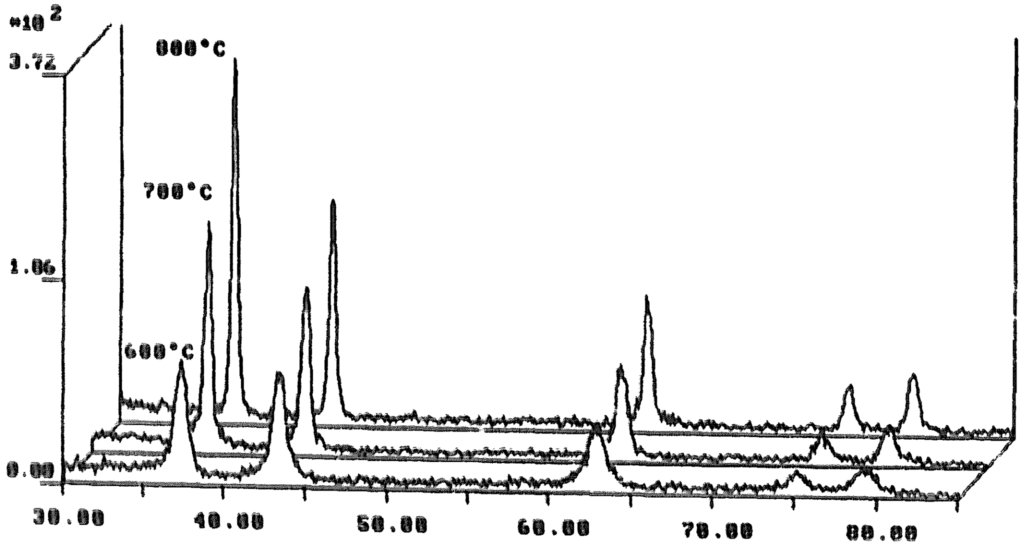

Fig. 4. XRD powder patterns corresponding to Ti(O,N) oxynitride phases prepared in the 600–800°C range.

color. XRD patterns of powders nitrided in the range 600–800°C are shown in Fig. 4. The peak broadening observed at 600°C is correlated to a poor crystallization state and to a small particle size. Indeed, a very high specific surface area ($S_g = 85$ m^2 g^{-1}) is obtained under these conditions. Table 4 gives the chemical composition of the powders as a function of temperature, as well as the cubic parameter value and the corresponding specific surface area. All the samples contain large amounts of oxygen, which demonstrates the oxophilic character of titanium, noted above. The oxygen content decreases with temperature whereas the unit cell parameter increases. Note also that the formal oxidation state of Ti, d_{OX} Ti, is close to 4 in the low temperature oxygen-rich oxynitride phases. It slowly decreases as T increases to reach a limit value of 3 in stoichiometric TiN which is expected to form, starting from pure TiS_2 and NH_3 (according to our recent results).

4. Conclusion

In this paper, the possibility to prepare nitride-type compounds from sulfides heated in flowing ammonia has been illustrated in the case of the transition elements tungsten, chromium and titanium. Ammonolysis of the corresponding sulfides WS_2, Cr_2S_3 (or $NaCrS_2$) and TiS_2 leads to nitrided phases with complete removal of sulfur as H_2S gas. Owing to this original preparation route, nitrides such as W_5N_6, or previously described Mo_5N_6, have been isolated for the first time as bulk materials. On the other hand the use, in particular, of non-dehydrated commercial ammonia evidences the oxophilic character of early transition metals, especially of titanium. Synthesis of pure nitride requires the use, in this case, of drastic purity conditions of the starting products. The sulfide route appears to be very promising for elaboration of more complex nitrides.

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