

# Synthesis of ternary nitrides by mechanochemical alloying

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Ternary metal nitrides (of general formula  $M_xM'_yN_z$ ) attract considerable interest because of their special mechanical, electrical, magnetic, and catalytic properties. Usually they are prepared by ammonolysis of ternary oxides ( $M_xM'_yO_m$ ) at elevated temperatures. We show that ternary transition metal nitrides are also obtained by nitridation of the corresponding ternary carbide at 823 K. This transformation appears to occur by solid-state diffusion of carbide and nitride ions. To establish more general synthesis schemes for ternary nitrides, we have focused on the preparation of ternary nitrides by mechanochemical alloying of a binary transition metal nitride ( $M_xN$ ) with an elemental transition metal. In this way, we have been able to prepare  $Fe_3Mo_3N$  and  $Co_3Mo_3N$  by ball-milling of  $Mo_2N$  with Fe and Co, respectively. The transformation sequence from the starting materials (the binary nitride and the transition metal) to the ternary nitride was followed by Mössbauer spectroscopy (for  $Fe_3Mo_3N$ ) and by X-ray powder diffraction (for both  $Fe_3Mo_3N$  and  $Co_3Mo_3N$ ). Usually, the preparation of a given ternary nitride by ammonolysis of a ternary oxide is dependent on the availability of an oxide precursor with the desired stoichiometric ratio of the two metals. In the present mechanochemical approach, this is not a prerequisite. These synthesis routes are expected to be applicable to the synthesis of a wide range of ternary compounds.

## 1 Introduction

Ternary metal nitrides (of the general formula  $M_xM'_yN$ ; M and M' being metals) are generally much less studied than ternary metal oxides or sulfides since they are usually obtained only under special reaction conditions. However, ternary nitrides and carbides have attracted considerable attention because of their special mechanical, electrical, magnetic and catalytic properties.<sup>1</sup> It has particularly been shown that  $Fe_3Mo_3N$ ,  $Co_3Mo_3N$  and  $Ni_2Mo_3N$  (often erroneously formulated as  $Ni_3Mo_3N$ ) are active ammonia synthesis catalysts, and the promoted catalyst Cs/ $Co_3Mo_3N$  is even more active than the traditional multi-promoted iron catalyst used for almost a century in industry.<sup>2,3</sup> These results have been paralleled by recent independent reports of the high catalytic activity of Cs/ $Co_3Mo_3N$  in ammonia synthesis<sup>4</sup> and of nickel molybdenum nitride catalysts in ammonia decomposition.<sup>5</sup> These ternary nitride-based ammonia synthesis and decomposition catalysts were prepared by ammonolysis of ternary oxide precursors at elevated temperatures. Also ternary carbide catalysts showed promise in reactions of industrial interest<sup>6,7</sup> but this is a new area and only a few studies have appeared. However, it seems that both ternary nitrides and carbides offer new possibilities compared to those given by the extensively studied binary materials.

Ternary carbides are usually prepared by carburization of the corresponding ternary oxide. So far, nitridation or carburization are the common approaches to the preparation of binary and ternary nitrides and carbides, respectively. Generally, many different ternary nitrides and carbides are available using this method. However, it is dependent on the availability of oxide precursors that have the same stoichiometric ratio of the two metals as that of the desired ternary nitride or carbide. Since ternary oxides often contain metals in relatively high oxidation states whereas in nitrides and carbides, the metals are present in low oxidation states, there

is no reason that oxides and nitrides/carbides should have the same stoichiometric ratio of metals. Consequently, nitridation and carburization of ternary oxides often lead to the formation of mixtures. This complicates the interpretation of the structural information and this is the reason why *e.g.*,  $Ni_3Mo_3N$  is claimed to form by ammonolysis of  $NiMoO_4$ .<sup>8</sup> However, it has been conclusively shown that a mixture of  $Ni_2Mo_3N$  and  $NiMo_x$  alloy results rather than  $Ni_3Mo_3N$ .<sup>3,9</sup>

Recently, it was shown that ternary carbides are available by a simple mechanochemical approach involving only high-energy ball-milling of the constituent elements, *e.g.*,  $\eta$ - $Fe_3Mo_3C$  is obtained by high-energy ball-milling of elemental iron, molybdenum and carbon.<sup>10,11</sup> It was also shown that the ternary nitride  $Fe_3Mo_3N$  could not be obtained by mechanochemical alloying of iron and molybdenum in a dinitrogen or ammonia atmosphere.<sup>10</sup> Therefore, we decided to investigate if ternary carbides could be transformed into ternary nitrides by nitridation as is possible for binary nitrides. However, in order to establish a general route to ternary nitrides, we also decided to attempt the preparation of ternary nitrides by mechanochemical alloying of a binary nitride with a metal. This would be a desirable route to ternary nitrides since a wide range of binary nitrides is prepared easily by ammonolysis of the corresponding binary oxides. Mechanochemical alloying has emerged as a versatile technique for producing materials such as amorphous alloys, nanostructured alloys, and metastable solid solutions.<sup>12–14</sup> We have shown that mechanochemical alloying provides a useful method for preparing conventional multi-promoted iron catalysts for ammonia synthesis with activities similar to the commercially available catalyst.<sup>15</sup> Although the principles governing these reactions in most cases are incompletely understood and undoubtedly also system specific, the formation of many compounds prepared by mechanochemical reactions, for example, borides,<sup>16</sup> nitrides and carbides<sup>10,11,17–22</sup> and silicides<sup>23,24</sup> have been reported.

## 2 Experimental

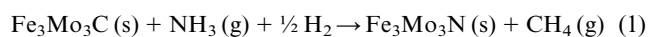
All reagents used were of analytical purity.  $\eta$ - $\text{Fe}_3\text{Mo}_3\text{C}$  was prepared by high-energy ball-milling of a mixture of the elements: Fe, Mo and C in the stoichiometric ratio as previously described,<sup>11</sup> tableted into pellets and crushed to a particle size of 0.3–0.5 mm. These granules were placed in a high-pressure reactor<sup>15</sup> and treated with a flow (20 normal  $\text{l g}^{-1} \text{h}^{-1}$ ) of 4.5% ammonia in 3:1 dihydrogen/dinitrogen at 100 bar and 823 K. It is necessary to transform the powder into granules to ensure proper plug flow conditions during the nitridation. Otherwise, powder samples would not experience the same, reproducible reaction conditions from experiment to experiment. The high flow is necessary to avoid all the ammonia decomposing immediately upon contacting the granules (*vide infra*). Samples were withdrawn at different intervals for characterization.

Molybdenum nitride ( $\gamma$ - $\text{Mo}_2\text{N}$ ) was obtained by ammonolysis of molybdenum oxide at 823 K according to the method reported by Lee *et al.*<sup>25</sup> Molybdenum nitride was carefully passivated by treatment with 1000 ppm dioxygen in dinitrogen at 293 K prior to exposure to ambient atmosphere. In agreement with the literature, this yielded a molybdenum nitride sample with a surface area of  $178 \text{ m}^2 \text{ g}^{-1}$  (BET-method) and an oxygen content of *ca.* 5–6 wt% (based on the Mo and N elemental analyses). This is a typical oxygen content for a passivated transition metal nitride. The oxygen content corresponds to an average coverage of the nitride crystals with a few layers of molybdenum oxide ( $\text{MoO}_2$  or  $\text{MoO}_3$ ). Molybdenum nitride was mixed with elemental Fe or Co in a molar ratio Mo:M (M = Fe, Co) of 1.0. The mixture was transferred to a planetary (Fritsch Pulverisette 5) ball-mill. The device consisted of nine tungsten carbide balls of diameter 20 mm, confined in a horizontal tungsten carbide vial. The milling speed was set at 200 rotations per minute, and the ball-to-powder ratio was 19:1. Samples were withdrawn from the ball-milling experiment after 0.5, 5, 10, 20, 40, 60, and 90 hours for characterization. After 90 hours of ball-milling, the powder was transferred to a quartz tube and annealed in argon (purity, 99.9999%) at temperatures of 773, 873, 923 and 973 K for 2 hours. The resulting samples were characterized by X-ray powder diffraction (XRPD) and the Fe-containing samples also by Mössbauer spectroscopy.

X-Ray powder diffraction patterns were obtained at room temperature with a Philips vertical powder diffractometer using  $\text{Cu-K}\alpha$  radiation. Mössbauer spectra were recorded at 295 K employing a constant acceleration type Mössbauer spectrometer in transmission geometry, and a 25 mCi  $^{57}\text{Co}$  source. The spectrometer was calibrated using  $\alpha$ -Fe foil at 295 K and the isomer shifts are given relative to  $\alpha$ -Fe at 295 K. Mössbauer spectra were fitted by a home-made least-squares fitting program with constrained pair width and intensity. For the sextet, an area ratio of 3:2:1 was applied.

## 3 Results and discussion

Fig. 1 shows the gradual transformation of  $\eta$ - $\text{Fe}_3\text{Mo}_3\text{C}$  to  $\text{Fe}_3\text{Mo}_3\text{N}$  by nitridation at 823 K with a partial pressure of ammonia of 4.5 bar. According to literature data, the ternary carbide and nitride both crystallize in the space group  $Fd\bar{3}m$  (no. 227). Thus, they are isomorphous with only slightly different unit cell sizes. From X-ray powder diffraction patterns obtained from the samples withdrawn during the experiment, it is however easily seen how the transformation occurs, most likely according to the tentative reaction scheme:



It is difficult to verify the role of  $\text{H}_2$  in the transformation because even if only  $\text{NH}_3$  is used as a reactant, some

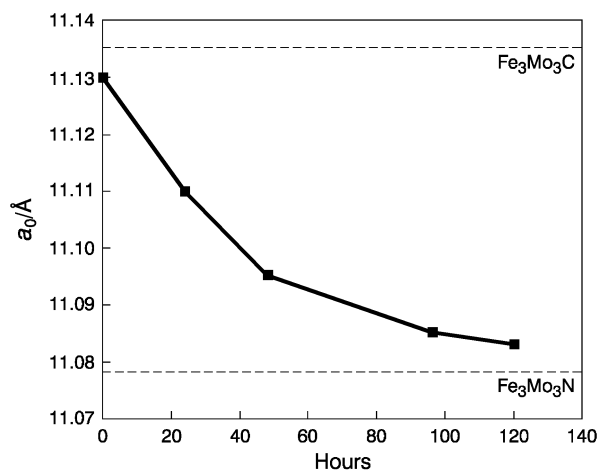
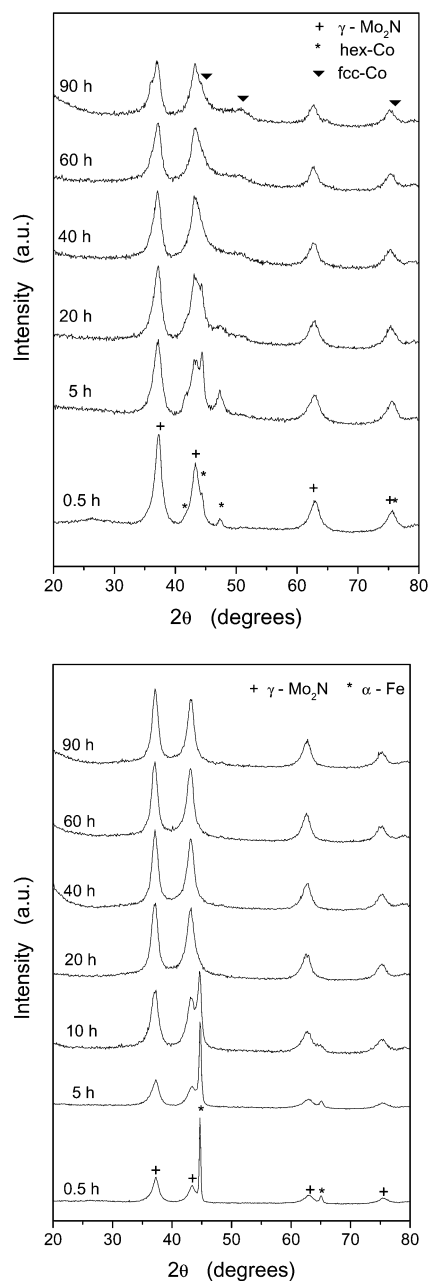


Fig. 1 Transformation of  $\eta$ - $\text{Fe}_3\text{Mo}_3\text{C}$  into  $\text{Fe}_3\text{Mo}_3\text{N}$  by nitridation at 823 K. The reaction is followed by the change of  $a_0$  since the ternary carbide and nitride are isomorphous with cubic lattice constants of 11.1355 and 11.0783 Å, respectively.

dihydrogen will form by ammonia decomposition, as  $\text{Fe}_3\text{Mo}_3\text{N}$  is an active ammonia synthesis and ammonia decomposition catalyst under these conditions. No changes in the X-ray diffraction line widths are observed during the transformation so it appears that the reaction occurs by solid-state diffusion of nitride and carbide ions. This is also the reason for the quite slow reaction; the complete transformation requiring at least 120 hours even at the relatively high temperature and high ammonia partial pressure used. The reaction would possibly be faster at higher temperatures due to increased diffusivity. However, at increased temperatures, the ammonia decomposition reaction becomes faster and the equilibrium concentration of ammonia lower. It is, of course, possible to use a pure ammonia gas for the reaction. However, due to the catalytic decomposition of ammonia, which is endothermic, a significant temperature gradient would result in the reactor. Therefore, the present reaction conditions represent a suitable compromise that is reproducible and allows complete conversion of the nitride. However, since this reaction is so slow and depends on the availability of carbide precursors with the desired stoichiometry, it is desirable to establish a more general synthesis route. Therefore, we pursued the mechanochemical reaction between a binary nitride and the elemental metal.

Fig. 2 shows the X-ray powder diffraction patterns obtained for the 2Fe:  $\text{Mo}_2\text{N}$  and 2Co:  $\text{Mo}_2\text{N}$  samples after 0.5, 5, 10, 20, 40, 60, and 90 hours of ball-milling. Note that the XRPD pattern of the sample milled for 0.5 h is the same as the initial powder mixture (not shown here). It is seen that the diffraction peaks of elemental Fe and Co gradually disappear whereas the diffraction peaks of  $\text{Mo}_2\text{N}$  remain almost unchanged. For the Co:  $\text{Mo}_2\text{N}$  sample, it is furthermore observed that prior to the disappearance of the cobalt diffraction peaks, the starting material, hexagonal Co, transforms into the high-temperature form, cubic cobalt. The powder diffraction patterns can be interpreted as the formation of a solid solution of Fe and Co in the oxygen-passivated molybdenum nitride. This is also supported by a slight increase of the lattice constant of molybdenum nitride during the ball-milling. For the 2Fe:  $\text{Mo}_2\text{N}$  sample, the lattice constant increases as evidenced by slight gradual shifts of the  $\text{Mo}_2\text{N}$  reflections during ball-milling.

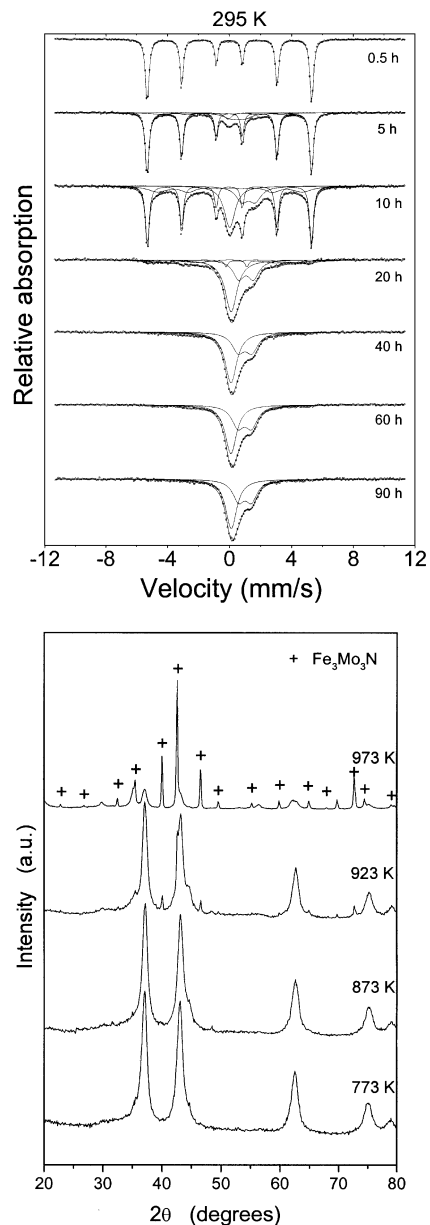
To ensure that the phase transformations observed could be solely attributed to a reaction between the nitride and the element, two reference experiments were conducted. Pure Fe and Co were milled under the same milling conditions and no amorphous-like phases were detected and only metallic elements remained. For the iron-containing sample, the conversion into a solid solution is also supported by the



**Fig. 2** XRPD patterns obtained from 2Fe:Mo<sub>2</sub>N and 2Co:Mo<sub>2</sub>N samples after different periods of ball-milling. After 90 hours, only the diffraction pattern of Mo<sub>2</sub>N remains. Prior to solubilization of Co in Mo<sub>2</sub>N, Co is transformed into the high-temperature cubic form.

Mössbauer spectra, shown in Fig. 3, which demonstrates that iron is transformed from the metallic state into another chemical environment as shown by the disappearance of the sextet characteristic of metallic Fe. The hyperfine parameters obtained from fitting the spectra of the samples are listed in Table 1.

For the sample milled for 0.5 hour, the Mössbauer spectrum could be fitted as a sextet with a hyperfine magnetic field of 32.9 T, which was identical to that of pure  $\alpha$ -Fe. After 5 hours of ball milling, the spectrum could be fitted to a broadened sextet (20.4 T and 6.2%), a doublet (5.0%) and a singlet (10.4%) together with the  $\alpha$ -Fe sextet (75.8%). On the basis of Mössbauer parameters,<sup>26,27</sup> the sextet with a magnetic field of 20.4 T might be attributed to the  $\gamma'$ -Fe<sub>4</sub>N phase while both the doublet and singlet may be due to the Fe–Mo–O–N solid solution. The possibility of forming an oxygen-containing phase is a consequence of the slight oxygen content introduced into the sample during passivation of the samples. It should be



**Fig. 3** Mössbauer spectra obtained from left) 2Fe:Mo<sub>2</sub>N samples after different periods of ball-milling. XRPD patterns obtained from right) 2Fe:Mo<sub>2</sub>N solid solution upon annealing at 773, 873, 923, and 973 K.

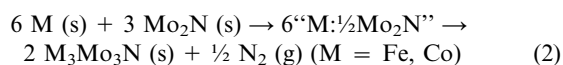
noted that the  $\gamma'$ -Fe<sub>4</sub>N phase has an fcc-structure, which is similar to  $\gamma$ -Mo<sub>2</sub>N from XRD patterns. After 10 hours, a new sextet with a hyperfine magnetic field of 29.0 T appeared to be characteristic of  $\alpha'$ -martensite phase. Chen and Williams<sup>26</sup> investigated the non-equilibrium phase transformation of mechanically alloyed Fe in NH<sub>3</sub> gas. During 405 hours of milling, the observed phase transformations were as follows:  $\alpha$ -Fe  $\rightarrow$   $\alpha'$ -martensite +  $\gamma$ -Fe  $\rightarrow$   $\gamma'$ -Fe<sub>4</sub>N  $\rightarrow$   $\epsilon$ -Fe<sub>2-3</sub>N. Here, it is also reasonable to believe that with increasing milling time, more and more  $\alpha$ -Fe diffused into and reacted with  $\gamma'$ -Fe<sub>4</sub>N to form  $\alpha'$ -martensite. After 20 hours of ball-milling, the spectrum of our sample could be fitted with a small sextet (3.8%) belonging to  $\alpha$ -Fe together with a doublet and a singlet for the Fe–Mo–O–N phase. It should be noted that the iron content in the Fe–Mo–O–N phase could change with milling time. Consequently, the Mössbauer parameters (IS and QS) of the doublet and the singlet listed in Table 1 changed slightly from 5 to 20 hours of ball-milling. For the samples ball-milled longer than 20 h, all the spectra display a doublet and a singlet with Mössbauer parameters identical to those of the sample milled for 20 hours.

**Table 1** Mössbauer parameters at 295 K, hyperfine fields  $H$  (T), isomer shifts IS ( $\text{mm s}^{-1}$ ) with respect to  $\alpha$ -Fe, quadrupole splitting QS ( $\text{mm s}^{-1}$ ), line width  $\Gamma$  ( $\text{mm s}^{-1}$ ) of the outer lines in sextets and relative resonance area RA (%) for the mixture of Fe and  $\gamma$ - $\text{Mo}_2\text{N}$  powders after various ball-milling times

Time/h	Component	$H$	IS	QS	$\Gamma$	RA
0.5	$\alpha$ -Fe	32.9	0	0	0.27	100
5	$\alpha$ -Fe	32.9	0	0	0.28	75.8
	MAF	20.4	0.28	-0.12	1.59	9.0
	<sup>a</sup> D	—	1.24	0.77	0.74	5.0
10	<sup>b</sup> S	—	0.05	—	0.89	10.4
	$\alpha$ -Fe	32.8	0	0	0.28	41.4
	<sup>d</sup> MAM	29.0	0.05	-0.01	1.51	21.1
	D	—	1.23	0.85	0.94	16.1
20	S	—	0.03	—	0.85	21.4
	$\alpha$ -Fe	32.5	-0.01	-0.03	0.29	3.8
	D	—	0.99	0.86	0.73	40.1
40	S	—	0.10	—	0.74	56.1
	D	—	0.99	0.88	0.97	43.4
60	S	—	0.09	—	0.90	56.6
	D	—	0.98	0.87	0.96	47.7
90	S	—	0.09	—	0.90	52.3
	D	—	0.98	0.85	0.89	47.8
	S	—	0.10	—	0.85	52.2

<sup>a</sup>D: the doublet component in the non-magnetic Mo-Fe-O-N solid solution. <sup>b</sup>S: the singlet component in the non-magnetic Mo-Fe-O-N solid solution. <sup>c</sup>MAF: magnetic amorphous  $\gamma$ - $\text{Fe}_3\text{N}$ -type phase. <sup>d</sup>MAM: magnetic amorphous  $\alpha'$ -martensite-type phase.

To understand the microscopic structures of the doublet and singlet for the solid solution more studies are required. The samples isolated after 90 hours of ball-milling were annealed at various temperatures in an atmosphere of dinitrogen for 2 hours, and the resulting XRPD patterns are shown in Fig. 3. The XRPD patterns for the samples annealed at 773 and 873 K can still be ascribed to the solid solution. New diffraction peaks, due to ternary nitride phase, appear at 923 K. The sample is dominated by the ternary nitride phase in the sample annealed at 973 K. The results indicate that it is necessary to heat the sample to 973 K for 2 hours to obtain the ternary nitride. A completely analogous behaviour is observed for the cobalt molybdenum nitride system. For  $\text{Fe}_3\text{Mo}_3\text{N}$ , this is independently supported by the Mössbauer spectra obtained from the same Fe-containing samples as discussed above. During the heat treatment, the singlet and doublet observed after 90 hours of ball-milling transform into a new singlet assigned to the ternary nitride. Consequently, formation of ternary nitrides can be achieved using a mechanochemical approach based on the following reaction scheme:



The first reaction proceeds during the ball-milling whereas the second reaction proceeds during the heat treatment. Formation of the ternary carbide,  $\text{Fe}_3\text{Mo}_3\text{C}$ , by ball-milling of the constituent elements occurs partially after 90 hours and the annealing procedure is only necessary to complete crystallization. Therefore, it appears that formation of the ternary nitride is more difficult, possibly because the starting material  $\text{Mo}_2\text{N}$  is less reactive than pure Mo. However, it seems that ball-milling of a binary nitride with an element provides a convenient synthesis route to ternary nitrides. Since a similar method can be used to prepare ternary carbides, it is possible that also ternary borides, silicides, oxides and sulfides, etc. can be similarly prepared. For many of these materials this would be a desirable preparative route since very few useful syntheses are known.

## 4 Conclusions

We have shown that ternary transition metal nitrides are obtained by nitridation of the corresponding ternary carbide at 823 K. This transformation appears to occur by solid-state diffusion of carbide and nitride ions. To establish more general synthesis schemes for ternary nitrides, we focused on the preparation of ternary nitrides by mechanochemical alloying of a binary transition metal nitride ( $\text{M}_x\text{N}$ ) with an elemental transition metal. In this way, we were able to prepare  $\text{Fe}_3\text{Mo}_3\text{N}$  and  $\text{Co}_3\text{Mo}_3\text{N}$  by ball-milling of  $\text{Mo}_2\text{N}$  with Fe and Co, respectively, followed by annealing. The transformation sequence from the starting materials (the binary nitride and the transition metal) to the ternary nitride was followed by Mössbauer spectroscopy (for  $\text{Fe}_3\text{Mo}_3\text{N}$ ) and by X-ray powder diffraction (for both  $\text{Fe}_3\text{Mo}_3\text{N}$  and  $\text{Co}_3\text{Mo}_3\text{N}$ ). Usually, the preparation of a given ternary nitride by ammonolysis of a ternary oxide is dependent on the availability of an oxide precursor with the desired stoichiometric ratio of the two metals. In the present mechanochemical approach, this is not a prerequisite. These synthesis routes are expected to be applicable to the synthesis of a wide range of ternary compounds.

## References

- S. T. Oyama, ed., *The Chemistry of Transition Metal Carbides and Nitrides*, Blackie Academic, London, 1996.
- C. J. H. Jacobsen, M. Brorson, J. Sehested, H. Teunissen and E. Törnqvist, *US Pat.*, 6,235,676, 1999, assigned to Haldor Topsøe A/S.
- C. J. H. Jacobsen, *Chem. Commun.*, 2000, 1057.
- R. Kojima and K. Aika, *Chem. Lett.*, 2000, 514.
- C. Liang, W. Li, Z. Wei, Q. Xin and C. Li, *Ind. Eng. Chem. Res.*, 2000, **39**, 3694.
- J. Patt, S. Bej and L. Thompson, *Proceedings of the 17th North American Catalysis Society Meeting*, Canada, 2001, p. 70.
- D. B. Dadyburjor, M. V. Iyer, E. L. Kugler and L. Norcio, *Proceedings of the 17th North American Catalysis Society Meeting*, Canada, 2001, p. 104.
- D. S. Bem, C. P. Gibson and H.-C. zur Loye, *Chem. Mater.*, 1993, **5**, 397.
- P. S. Herle, M. S. Hegde, K. Sooryanarayana, T. N. G. Row and G. N. Subbanna, *Inorg. Chem.*, 1998, **37**, 4128.
- L. M. Di, A. Calka, Z. L. Li and J. S. Williams, *J. Appl. Phys.*, 1995, **78**, 4118.
- J. J. Zhu, J. Z. Jiang, C. J. H. Jacobsen and X. P. Lin, *J. Mater. Chem.*, 2001, **11**, 864.
- W. L. Johnson, *Prog. Mater. Sci.*, 1986, **30**, 81.
- C. C. Koch, in *Materials Science and Technology*, R. W. Cahn, P. Hassen and E. J. Kramer, eds., vol. 15, VCH, Weinheim, Germany, 1991, p. 193.
- J. Z. Jiang, C. Gente and R. Bormann, *Mater. Sci. Eng.*, 1998, **A242**, 268.
- C. J. H. Jacobsen, J. Z. Jiang, S. Mørup, B. S. Clausen and H. Topsøe, *Catal. Lett.*, 1999, **61**, 115.
- L. Schutz, J. Wecker and E. Hellstern, *J. Appl. Phys.*, 1987, **61**, 3583.
- P. Matteazi and G. Le Caër, *J. Am. Ceram. Soc.*, 1991, **74**, 1382.
- A. Calka and J. S. Williams, *Mater. Sci. Forum*, 1992, **88-90**, 787.
- W. Y. Lim, M. Hida, A. Sakakibara, Y. Takemoto and S. Yokomizo, *J. Mater. Sci.*, 1993, **28**, 3463.
- G. M. Wang, S. J. Campbell, A. Calka and W. A. Kaczmarek, *J. Mater. Sci.*, 1997, **32**, 1461.
- P. Rochegude and J. Foct, *C. R. Acad. Sci., Ser. II*, 1989, **309**, 1545.
- R. S. de Figueiredo, J. Foct, A. V. dos Santos and C. A. Kuhnen, *J. Alloys Compd.*, 2001, **315**, 42.
- R. K. Viswanadham, S. K. Mannan and S. Kumar, *Ser. Metall.*, 1988, **22**, 1011.
- G. Tschakarov and G. Gospodinov, *J. Solid State Chem.*, 1985, **59**, 265.
- J. S. Lee, S. T. Oyama and M. Boudart, *J. Catal.*, 1987, **106**, 125.
- Y. Chen and J. S. Williams, *Mater. Sci. Eng.*, 1997, **A226-228**, 38.
- J. Foct and R. S. de Figueiredo, *Nanostruct. Mater.*, 1994, **4**, 685.