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Ternary metal nitrides by the urea route

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Abstract

Interstitial molybdenum ternary nitrides, M_nMo_3N (M = Fe and Co, $n = 3$; M = Ni, $n = 2$), can be obtained by heating the molybdate precursors, $FeMoO_4$, $CoMoO_4$ and $NiMoO_4$ with urea in the 1:12 molar ratio in the 900–1000 °C range. Fe_3Mo_3N and Co_3Mo_3N are obtained in pure form. The nickel nitride has the composition Ni_2Mo_3N and therefore is in admixture with nickel. All the nitrides have been characterized by various physical methods.

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1. Introduction

Ternary metal nitrides, such as alkaline earth silicon nitrides ($MSiN_2$ with M = Ba, Sr, Ca), alkaline earth zinc nitrides (Sr_2ZnN_2, Ba_2ZnN_2) and nickel nitrides (Sr_2 NiN_2 and CaNiN) have been synthesized by various means. One of the general procedures involves reacting a transition metal or a main group metal with an alkali or alkaline earth nitride or amide [1–4]. An approach to synthesize ternary nitrides of the type MWN_2 (M = Fe, Ni, Co) has been to heat the respective ternary oxide precursor in NH_3 [5–7]. The first metallic layered nitride, $LiMoN_2$, was synthesized by the ammonolysis of either a molecular organometallic precursor or a ternary oxide [8]. Weil and Kumta [9] reported the synthesis of Fe_3Mo_3N, $FeWN_2$, Ni_3Mo_3N and Ti_3AlN using complex precursors. Synthesis of Fe_3Mo_3N by the ammonolysis of the oxide precursor has been reported [10]. The ternary nitride, Ni_2Mo_3N, has been prepared by heating a metallorganic precursor in NH_3 [11]. Alconchel et al. [12] have reported a study on the influence of preparative variables on the ammonolysis of the molybdate precursors. Both the ammonolysis as well as the plasma nitridation of $FeMoO_4$ and $CoMoO_4$ results in the respective intermetallic nitrides [13]. Synthesis of Fe_3Mo_3N and Co_3Mo_3N by mechanochemical alloying and by the nitridation of the corresponding ternary carbide has also been reported [14]. Prior et al. [15,16] have reported the synthesis of $Ni_{2-x}M_xMo_3N$ (M = Co, Pd) and $Fe_{2-x}M_xMo_3N$ (M = Ni, Pd, Pt) by heating a stoichiometric mixture of the respective oxides under flowing synthesis gas.

Based on our recent success with the urea route to synthesize binary metal nitrides, such as BN, TiN and NbN [17], we decided to examine whether this simple procedure can also be used to produce ternary nitrides. In this article, we report the synthesis of interstitial molybdenum ternary nitrides, M_nMo_3N (M = Fe and Co, $n = 3$; M = Ni, $n = 2$) by the reaction of the respective ternary metal oxides with urea.

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2. Experimental

Hydrated metal molybdates were prepared by the dropwise addition of 400 mL (0.25 M) of an aqueous solution of the metal chloride ($FeC1_2$, $CoCl_2$ or $NiC1_2$) to a 150-mL (0.55 M) $Na_2MoO_4\cdot(H_2O)_2$ solution, and the solution stirred for 2 h to ensure completion of the reaction. The solid product was isolated by vacuum filtration and rinsed with two washings of water followed by a washing with ethanol. The solid was air-dried overnight followed by a drying at 150 °C for 24 h. The products were amorphous and had brown, violet and green colors in the case of $FeMoO_4$, $CoMoO_4$ and $NiMoO_4$, respectively.

To obtain crystalline ternary nitrides, a mixture of the respective oxide precursor and urea in the 1:12 molar ratio was taken in an alumina boat, placed in quartz tube and heated at 900 °C for 3 h in a N_2 atmosphere and the product quenched to room temperature. When the reaction was performed at 750 °C we obtained the nitrides, but the products were not completely crystalline.

The products formed in the above reactions were characterized by following techniques. X-ray diffraction (XRD) patterns were recorded using Cu Kα radiation on a Rich-Siefert XRD-3000-TT diffractometer. Scanning electron microscope (SEM) images were obtained using a LEICA S440i SEM. Mössbauer spectra were recorded using a Wissel spectrometer. The spectrum was recorded at room temperature using a ^{57}Co source. The isomer shift is reported relative to metallic iron at room temperature.

Electrical resistivity of the nitride samples were measured using four probe technique from 50 to 300 K.

3. Results and discussion

On heating a 1:12 mixture of $FeMoO_4$ with urea, Fe_3Mo_3N with the cubic eta carbide structure was obtained. It is isostructural with η-Fe_3W_3C. The XRD pattern shown in Fig. 1(a) confirms the formation of Fe_3Mo_3N ($a = 11.0620$ Å, JCPDS card no: 48–1408). Fig. 2(a) shows a SEM image of sub-micrometer particles of Fe_3Mo_3N. The Mössbauer spectrum of Fe_3Mo_3N measured at room temperature is shown in Fig. 3. The spectrum shows a symmetric single line with an isomer shift of 0.213 mm s^{-1} characteristic of Fe_3Mo_3N as reported in the literature [10,18]. The structure of Fe_3Mo_3N has iron atoms occupying the sites between the (NMo_6) octahedra which are corner-shared. By heating a 1:12 mixture of $CoMoO_4$ and urea, we obtained Co_3Mo_3N showing a XRD

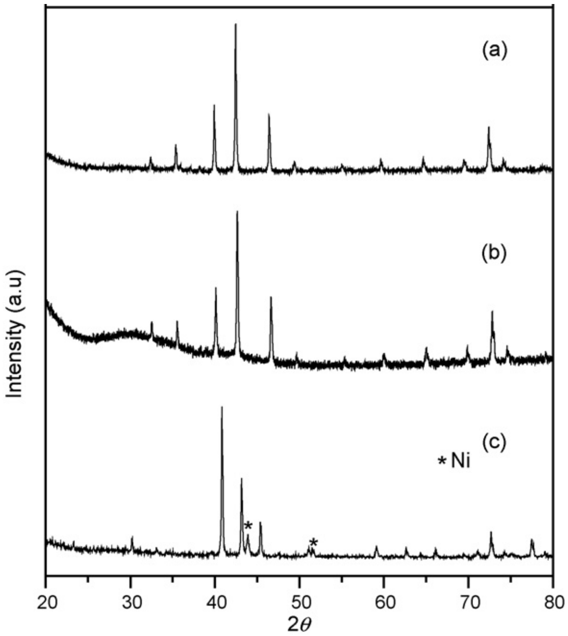

Fig. 1. XRD patterns of (a) Fe_2Mo_3N (b) Co_3Mo_3N (c) Ni_2Mo_3N.

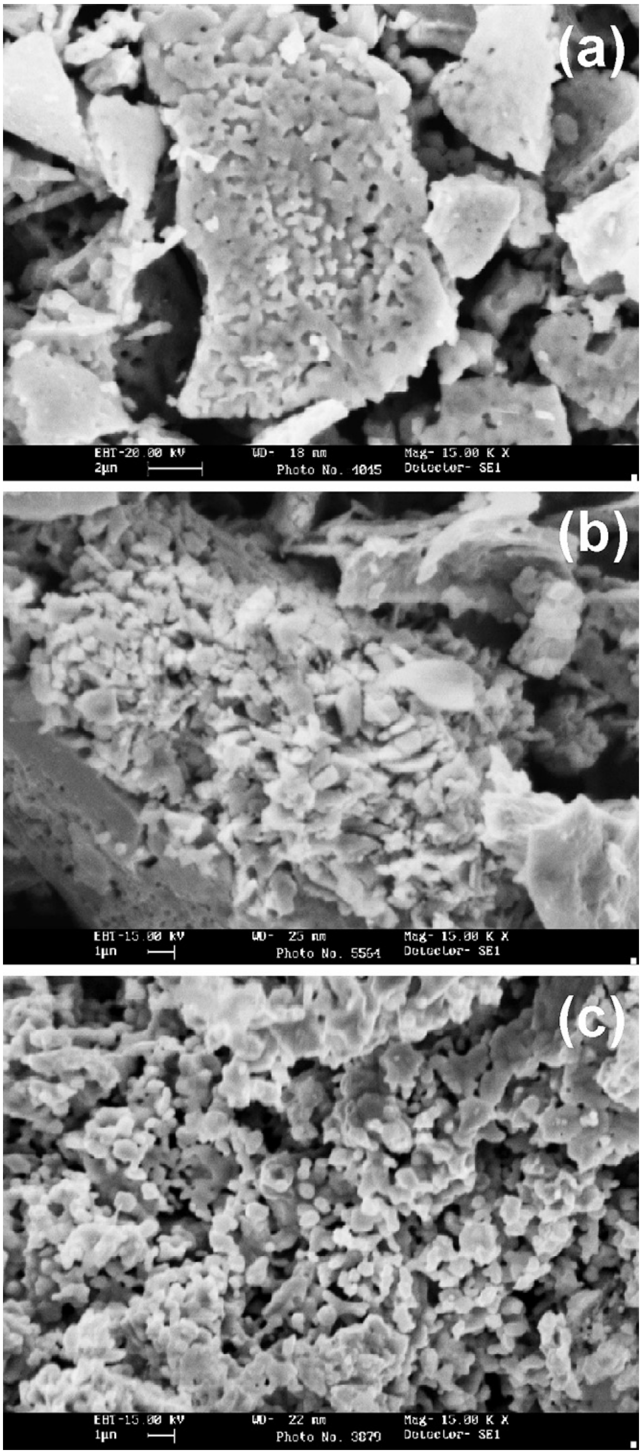

Fig. 2. SEM images of (a) Fe_2Mo_3N (b) Co_3Mo_3N (c) Ni_2Mo_3N.

pattern characteristic of cubic eta carbide structure (Fig. 1(b)), with a cell parameter of 11.0134 Å [11]. The product consisted of sub-micrometer sized particles as revealed by the SEM image in Fig. 2(b). The nitride was metallic as shown by the measurement of the temperature variation of resistivity (Fig. 4). The magnetic susceptibility data of the two nitrides agree well with literature [10,13] with Co_3Mo_3N showing a non-Curie like

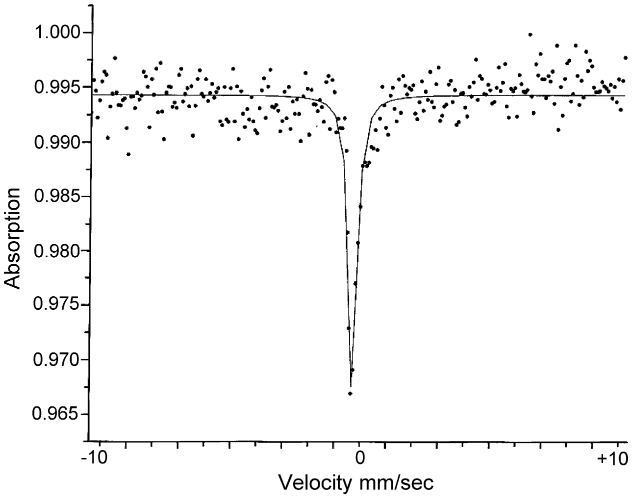

Fig. 3. Mössbauer spectrum of Fe_3Mo_3N.

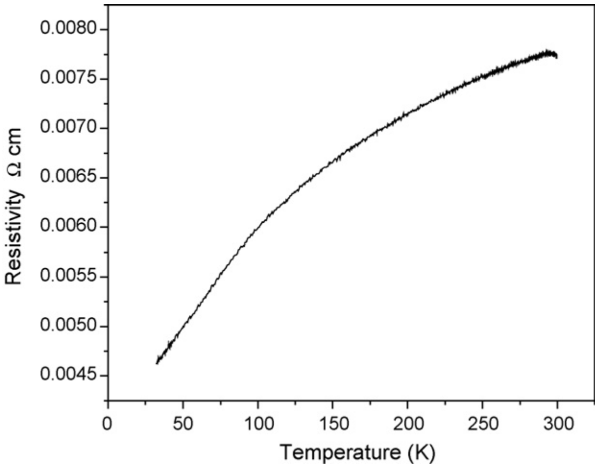

Fig. 4. Variation of resistivity, ρ, of Co_3Mo_3N with temperatures.

and Fe_3Mo_3N showing a Curie behavior. The reactions involved in the formation of Fe_3Mo_3N and Co_3Mo_3N is likely to be (1):

$$3CoMoO_4 + 8NH_3 \rightarrow Co_3Mo_3N + 12H_2O + 7/2N_2 \quad (1)$$

Here, NH_3 is generated by the decomposition of urea.

On heating a 1:12 mixture of $NiMoO_4$ with urea we obtained a mixture of Ni_2Mo_3N and Ni. The XRD pattern of the product shown Fig. 1(c) confirms the formation of cubic Ni_2Mo_3N ($a = 6.9001$ Å) and reveals the presence of nickel impurity as required by the reaction (2).

$$3NiMoO_4 + 8NH_3 \rightarrow Ni_2Mo_3N + Ni + 12H_2O + 7/2N_2 \quad (2)$$

The structure of Ni_2Mo_3N is similar to that of Al_2Mo_3C with a filled β-Mn structure. The SEM image shown Fig. 2(c) shows sub-micrometer sized particles. The presence of nickel was ascertained by magnetic measurements which showed ferromagnetism.

4. Conclusions

In conclusion, we have been able to prepare three ternary nitrides of type M_nMo_3N ($n = 3$ with M = Fe and Co and $n = 2$ with M = Ni) by a simple reaction of the precursor molybdates with urea.

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