

PRODUCTION OF DISPERSED MOLYBDENUM NITRIDE AND CARBIDE NANOSTRUCTURED CRYSTALLITES USING ULTRASONIC IRRADIATION

Leroy Covington, Jr. and Kenneth L. Roberts
Department of Mechanical and Chemical Engineering
North Carolina A&T State University
Greensboro, NC 27411-0001

ABSTRACT

Molybdenum nitride (γ -Mo₂N) has been previously examined by this group for hydrodesulfurization (HDS) catalysis due to its relatively high resistance to sulfur poisoning and ample surface area [1]. Mo₂N nanoparticles synthesized by this group using an ultrasonic dispersion method have been observed in the 4 to 15 nm range from TEM and STM measurements [2]. The excellent mechanical and thermal resistance properties of transition metal nitrides and carbides make them desirable as potential nanofiller materials for high strength, flame-resistant nanocomposites. Powders of molybdenum nitride (γ -Mo₂N) and molybdenum carbide (α -Mo₂C) were prepared by means of the temperature programmed reaction (TPR) method. Mo₂N was produced by the TPR of molybdenum (VI) oxide (MoO₃) and a reactant gas mixture of nitrogen/hydrogen. Mo₂C was synthesized in similar fashion by reacting MoO₃ with a pre-selected molar ratio of methane/hydrogen gas mixture. Dispersed nanostructured crystallites of Mo₂N and Mo₂C were produced via ultrasonic irradiation. Ultrasonic dispersion was employed by creating slurries of the metal nitrides and carbides with de-ionized water and subjecting the samples to ultrasound energy by means of an ultrasonic horn. Samples have been characterized using room temperature X-ray Diffraction (RTXRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM).

INTRODUCTION

Porous nanostructured γ -Mo₂N and β -Mo₂C have been synthesized by several investigators using temperature-programmed reaction (TPR) of MoO₃ and NH₃ [3-5], N₂/H₂ mixtures [2,6] and CH₄/H₂ mixtures [7]. Techniques utilizing ultrasonic reactions of molybdenum carbonyl in organic solvents for the synthesis of β -Mo₂C and other metal carbides have also been developed in parallel by other investigators [8,9]. Both the molybdenum nitride and carbide forms have been examined as catalysts for numerous industrial reactions [10-17]. Previous work from this group reported the synthesis of γ -Mo₂N nanoparticles from the ultrasonic dispersion of porous nanostructured γ -Mo₂N obtained from the TPR of MoO₃ with N₂/H₂ gas mixtures [2].

EXPERIMENTAL METHODS

Temperature Programmed Reaction Synthesis

Powders of molybdenum nitride and molybdenum carbide were synthesized using methods previously reported [18]. Approximately 0.1 g of MoO₃ powder (Aldrich, 99.5+%) was loaded into a stainless steel tube fitted with a porous silica wool and reacted in flowing N₂ (Air Products and Chemicals, Inc, Research Grade) / H₂ (National Welders, Ultra High Purity Grade) or CH₄ (Air Products and Chemicals, Inc., CP Grade) / H₂ at atmospheric pressures,

using gas flow procedures and the temperature program methods previously described using a Barnstead/Thermolyne Tube Furnace (Model F79345) with multi-programmable control. After the reaction was completed, the reactant gas was allowed to continue flowing and the products were cooled to room temperature. After cooling, the reactant gas flow was halted and the solid product was passivated using air that contacted the product sample through 0.5 m of 0.635 cm I.D. tubing for 24 h.

Ultrasonic Dispersion

Approximately, 50 mg of the nitride or carbide material was placed in 50 ml of 11.2 MΩ-cm deionized water to form a solid-liquid slurry. The deionized water was prepared by a Corning Mega Pure System *DF* using Barnstead Ultra-High Purity Disposable Deionizer Cartridges. The solid-liquid mixtures were next placed in a solid-state ultrasonic bath (L&R Manufacturing, Model T-28B) and sonicated for 15-30 minutes. A portion of the ultrasonically dispersed solution was extracted immediately following sonication and allowed to settle over a period of 96 to 168 hours. After settling, the resulting liquid was extracted once more and the remaining solids were dried under vacuum at 398 K for 4 to 5 hours.

Materials Characterization

X-ray diffraction analyses were performed using a Bruker D8 ADVANCE Series-2 X-ray diffractometer (Bruker AXS) equipped with a CuK α radiation source ($\lambda = 1.54 \text{ \AA}$). Data acquisition, diffraction pattern identification, and plot evaluation were accomplished using Diffractomaster installed on Dell Pentium 4 workstation interfaced to the diffractometer. The nitride and carbide powder samples were ground as required and mounted on a 1 square-inch glass slide using two-sided adhesive tape. The glass slide was then mounted on the analysis platform for evaluation. XRD measurements were collected using a 0.05 degree step size and a scan speed of 0.5 scans per second. The average crystallite sizes were estimated based on the peak-widths using the Scherrer equation [19]:

$$d_{hkl} = \frac{0.9\lambda}{B \cos \theta} \quad (1)$$

where d_{hkl} = diameter of crystal particle, B = broadening of diffraction line (peak width) measured at half its maximum intensity (radians), θ = is the angle of diffraction and λ is the incident radiation wavelength. The peak width was taken as the full width at half maximum intensity of the most intense peak assigned to the particular phase.

Surface morphology of the molybdenum nitrides and carbides was observed using a Hitachi Model S3000 N Variable Pressure Scanning Electron Microscope (Oxford Instruments). Scanning electron micrographs were collected with a Hitachi Superscan Elite 641 model computer that interfaced with the microscope. A small amount of the nitride and carbide powders were mounted on a Cu strip adhered to the SEM chamber support. The support was placed into the electron beam path for analysis. The vacuum was allowed to stabilize before analysis occurred.

RESULTS

Mo₂N powders were prepared from solid-gas phase reduction and nitridation reaction using the gaseous mixture of N₂/H₂ at atmospheric pressures with a predetermined temperature program. The starting material has flat needle-like morphology. The final product

of the reduction, nitridation, and passivation processes had a metallic dark-gray material composed of small particles (or crystallites) as shown in Figure 1.

Mo₂N nanoparticles were prepared by adding 50 ml of deionized water to 50 mg of powder and sonicated for 15 to 30 minutes. Addition of the water to the Mo₂N created an opaque dark gray to black solution. As the solution settled over a period of 7 days, the particles collected on the bottom of beaker and aqueous solution turned deep-blue and clear.

RTXRD was used in order to confirm the identity of this product as γ -Mo₂N with a tetragonal crystal lattice. The subsequent patterns were identified by comparison with the Powder Diffraction Files (PDF) of the International Centre for Diffraction Data (ICDD), formerly the Joint Committee on Powder Diffraction Standards (JCPDS). The XRD of the Mo₂N patterns display a very similar pattern as shown in Figure 1 with the most intense peaks occurring at diffraction angles, $2\theta = 37.60^\circ$ and 43.05° which corresponds to the (112) and (200) reflection planes, respectively. Scherrer analysis revealed average Mo₂N crystallite sizes were slightly larger than 24 nm in the (200) direction and smaller than 21 nm in the (112) direction. The ultrasonically dispersed Mo₂N nanoparticles were compared to undispersed Mo₂N crystallites by XRD to ensure that no change in the physical structure had taken place.

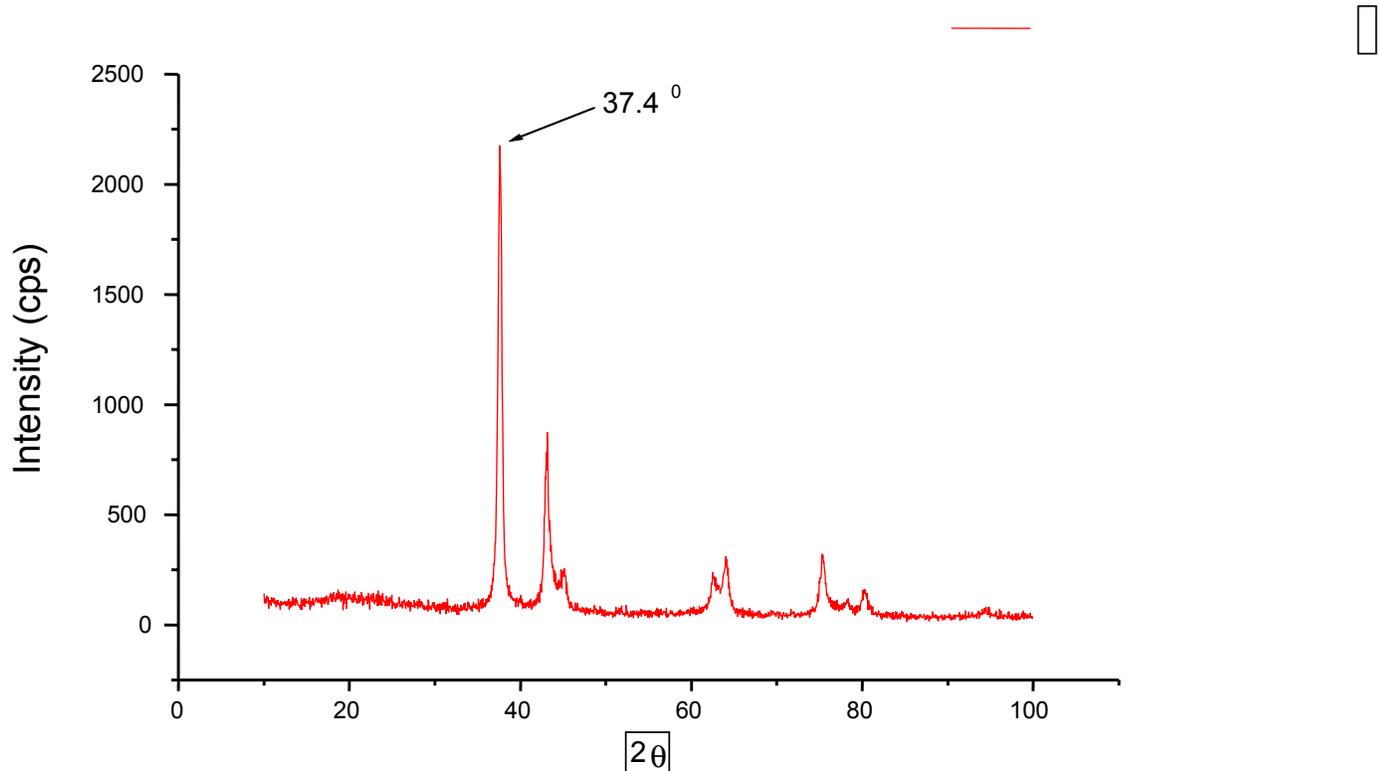


Figure 1: RTXRD of γ -Mo₂N Nanostructured Powder

A series of molybdenum carbides was prepared by the temperature programmed reduction/carburization of MoO_3 with a preselected mixture of CH_4/H_2 . The materials resulting from CH_4/H_2 synthesis were identified through XRD as a hexagonal form of $\alpha\text{-Mo}_2\text{C}$. These powders were composed of grayish-metallic crystallites. Using RTXRD, the only crystalline phase observed in this carbide group was Mo_2C . X-ray reflections found at 39.4° , 37.4° , and 34.4° correspond to (101), (002), and (100) planes, respectively. Average crystallite size is approximately 10.5 nm in the (101) direction, larger than 10 nm in the (002) direction and slightly smaller than 14 nm in the (100) direction.

During the preparation of Mo_2C via ultrasonic dispersion an interesting occurrence was noticed. Unlike the preparation of the Mo_2N , when Mo_2C was contacted with 50 ml of deionized water and sonicated for 15 to 30 minutes to form a slurry, the surface of the mixture formed a opaque metallic-silver layer with the consistency of silver paint. Stirring the mixture had no effect as the silver layer continued to stay suspended on top of the solution. Subjecting the mixture to rigorous agitation using a touch mixer, dissipated the bulk of the opaque layer, however a more diluted layer formed, only partially covering the surface of the aqueous solution.

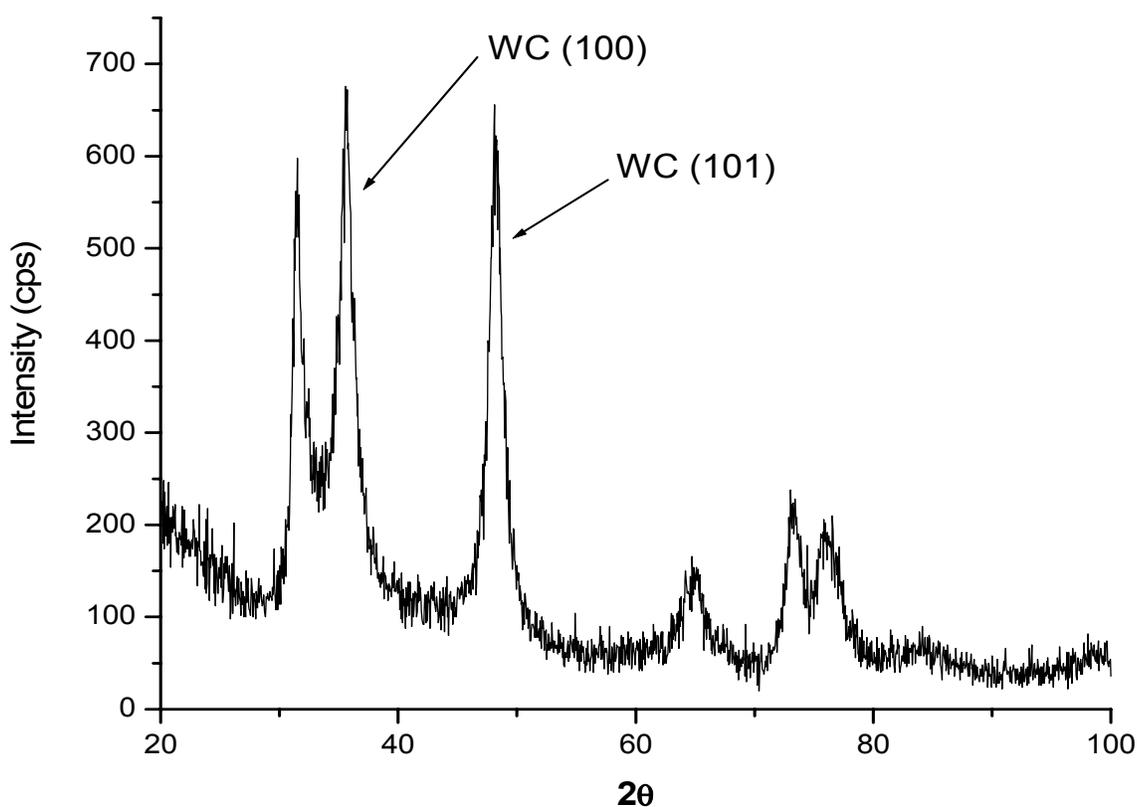


Figure 2: RTXRD of $\alpha\text{-Mo}_2\text{C}$ Nanostructured Powder

During sonication, individualized waves were observed to move throughout the mixture. These actions were most visible by looking down into the solution as the jet waves could be seen impeding the opaque viscous layer. Immediately after sonication, the solution was noticed to continue a “swirling” action and was opaque and grayish-black in color. Over a

period of several days of settling, the aqueous solution became clear and dark-blue as the nanoparticles settled out. Comparison of the sonicated Mo₂C with the undispersed Mo₂C by means of RTXRD indicated that the bulk phase was Mo₂C as shown in Figure 2.

CONCLUSIONS

Porous molybdenum nitride and carbide were produced as confirmed by RTXRD using temperature programmed reaction of molybdenum trioxide with gaseous mixtures of N₂/H₂ and CH₄/H₂, respectively. Dispersed nanostructured crystallites of γ -Mo₂N and α -Mo₂C were produced by means of ultrasonic irradiation. RTXRD confirmed the identity of the molybdenum compounds before and after ultrasonic dispersion. Slight increases in the ranges of nanocrystallite sizes were observed for both molybdenum materials. This may have been a result of the bubble formation, growth and implosion mechanics for aqueous ultrasonics.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the support of the United Negro College Fund Special Programs-Department of Defense Grant number W911NF-04-1-0045 for financial assistance, the Graduate Degrees for Minorities in Engineering and Science (GEM) Fellowship Program and Air Products & Chemicals, Inc., the Center for Composite Materials Research (CCMR) at North Carolina A&T State University, and the Center for Advanced Materials and Smart Structures (CAMSS) at North Carolina A&T State University.

REFERENCES

1. Markel, E.J., Burdick, S.E., Leaphart, M.E., III, and Roberts, K.L., *J. Catal.*, **182**, 136 (1999).
2. Roberts, K.L. and Markel, E.J., *J. Phys. Chem.*, **98**, 4083 (1994).
3. Volpe, L. and Boudart, M., *J. Solid State Chem.*, **59**, 332 (1985).
4. Ranhorta, G.S., Haddix, G.W., Bell, A.T., and Reimer, J.A., *J. Catal.*, **108**, 24 (1987).
5. Choi, J-G, Curl, R.L., and Thompson, L.T., *J. Catal.*, **146**, 218 (1994).
6. Wise, R.S. and Markel, E.J., *J. Catal.*, **145**, 335 (1994).
7. Lee, J.S.; Oyama, S.T.; and Boudart, *J. Catal.*, **106**, 125 (1987).
8. Suslick, K.S.; Hyoen, T.; Fang, M.; and Cichowlas, A.A., *Matl Sci & Eng.*, **A204**, 186 (1995).
9. Mahajan, D.; Papish, E.T.; and Pandya, K., *Ultrasonics Sonochemistry*, **11**, 385 (2004).
10. Volpe, L. and Boudart, M., *J. Phys. Chem.*, **90**, 4878 (1986).
11. Wise, R.S. and Markel, E.J., *J. Catal.*, **145**, 344 (1994)
12. Ranhorta, G.S., Bell, A.T., and Reimer, J.A., *J. Catal.*, **108**, 40 (1987).
13. Oyama, S.T., *Catal. Today*, **15**, 279 (1992).
14. Schlatter, J.C., Oyama, S.T., Metcalfe, J.E., and Lambert, J.M., *Ind. Eng. Chem. Res.*, **27**, 1648 (1988).
15. Choi, J-G, Brenner, J.R., Colling, C.W., Demczyk, B.G., Dunning, J.L., and Thompson, L.T., *Catal. Today*, **15**, 201 (1992).
16. Markel, E.J. and Van Zee, J.W., *J. Catal.*, **126**, 643 (1990).

17. Nagai, M., Miyao, J., and Tsuboi, T., *Catal. Lett.*, **18**, 9 (1993).
18. Choi, J-G, Brenner, J.R., and Thompson, L.T., *J. Catal.*, **154**, 33 (1995).
19. Cullity, B., Elements of X-Ray Diffraction, Phillipines: Addison-Wesley Publishing Co. (1978)