

High Surface Area Mo₂C and WC Prepared by Alkalide Reduction

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α -Mo₂C (orthorhombic) and α -WC (hexagonal) nanoparticles have been synthesized by subambient alkalide reduction. The initial products appear to be either amorphous or subnanocrystalline. Annealing above 575 and 1100 °C respectively resulted in X-ray crystalline material. The α -Mo₂C nanoparticles were found to have an average particle diameter of 3.1 nm by TEM with a narrow, log-normal distribution. Surface areas of as high as 229 m²/g were observed by the BET method. The α -WC nanoparticles were found to have a much broader size distribution with particles ranging from ~3 to 50 nm. Surface areas were found to be as high as 140 m²/g.

Introduction

Current interest in carbides with small particle size and high surface area is in no small part due to their potential applications in ceramic science and catalysis. Interstitial transition metal carbides are extremely hard, inert, and refractory materials. Unfortunately, they are also brittle and difficult to machine. Finely divided carbide materials promise to allow the consolidation of fully dense solids with excellent fracture resistance for use in high stress and temperature applications such as in engine components where increased operation temperature could translate into tremendous economic advantage. As catalysts, carbides promise to be an inexpensive alternative to the noble metals with possibly even superior properties due to their ability to withstand high temperatures and resistance to poisoning. Interest in transition metal carbides as catalysts has grown steadily since it was first noted that tungsten carbide showed catalytic properties similar to those of platinum.¹ Subsequent studies have found favorable catalytic properties in a number of carbides, including Mo₂C, which is often compared to Ru and along with WC is probably the most often studied.

Traditionally, transition metal carbides have been made by high-temperature powder metallurgical techniques, which is energy intensive and results in large (micrometers) grains of low specific surface area. For example, WC is commercially manufactured by reaction of elemental starting materials at 2800 °C. Methods that achieve high surface area, preferably at considerably reduced processing temperature, are necessary for carbides to fulfill their promise in ceramic and catalytic applications.

A number of methods have been reported capable of the synthesis of high surface area Mo₂C and WC including gas-phase reactions,^{2,3} gas–solid reactions,^{4–9}

or electrochemical¹⁰ and solution state methods.^{11–14} Particularly high surface areas (50–200 m² g⁻¹) have been achieved by converting solution-derived precursors to the respective carbides,¹⁴ reaction of MoO₃ or WO₂ vapors with activated carbon,^{8,9} and sonochemical methods.¹¹

Alkalides are crystalline ionic salts consisting of crown ether or cryptand complexed alkali metal cations charged balanced by a stoichiometric number of alkali metal anions.^{15,16} Alkalides produce alkali metal anions when dissolved in nonreducible solvents. The alkali metal anion is nearly as thermodynamically powerful a reductant as a solvated electron, the most powerful reductant possible in any given solvent, and is capable of simultaneous two electron transfers. Alkalide reduction of metal salts results in the formation of a colloid of nanoscale (~2–15 nm diameter) particles. Colloid stability varies from minutes to hours, depending on the metal reduced and the reaction conditions. Following aggregation and removal of the solvent, the byproducts can be washed away, recovering the crown ether and leaving bare metal nanoparticles. Supported as well as bare particles can be produced.^{17–20}

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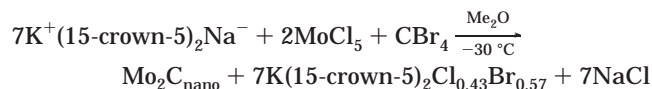
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Alkalide reduction has been shown capable of producing alloys and compounds by coreduction of two metals. In addition, the nanoscale metals have been used as precursors in nitride synthesis.²¹ Here we extend the method to the coreduction of metals with nonmetals to form compounds. Specifically, we show that the method is capable of producing high surface area α -Mo₂C and α -WC by coreduction of the respective metal cation and CBr₄.

Experimental Section

Nanoscale Mo₂C and WC were synthesized by homogeneous alkalide reduction according to the following scheme:



Note, the assignment of the Br⁻ in the byproducts is based on the lack of observed NaBr in X-ray patterns of unwashed samples; however, its inclusion in a mixed chloride/bromide crown ether complex phase is by no means certain. Dimethyl ether (Me₂O) and tetrahydrofuran (THF) were the solvents for Mo₂C and WC synthesis, respectively. MoCl₅, WCl₅ (both anhydrous, 99.9+%, packed under argon), and CBr₄ (99%) were purchased from Aldrich and used without further purification. Crown ether (15-crown-5, 98%) was purchased from Alfa-AESAR, further dried, and then purified by vacuum distillation. Dimethyl ether (Me₂O, C.P. grade, 99.8%, MG Industries) was purified by stirring over Na/benzophenone at -80 °C until a persistent blue solution was obtained. Tetrahydrofuran (THF, 99.9+% HPLC grade, inhibitor free) was purified by stirring over KNa alloy until a persistent blue solution was obtained. NH₃ (99.99% anhydrous grade, MG Industries), used as a wash solvent to remove byproducts, was purified by vacuum distillation from Na metal. All reactant and product manipulation was performed in a N₂-filled drybox (<1 ppm H₂O and O₂), and solvent transfers were accomplished by vacuum techniques (10⁻⁶ Torr). Sample annealing was done in fused-silica tubing flame-sealed under vacuum (10⁻⁶ Torr). Further synthetic details can be found elsewhere.¹⁷⁻²¹

Electron micrographs were obtained on a JEM-1200EX transmission electron microscope (TEM) operation at 60 and 80 keV. Samples for TEM were dispersed in MeOH by sonication and deposited on Formvar holey film/carbon-coated copper grids. Powder X-ray patterns were obtained with a Scintag XDS-2000 diffractometer with Cu K α radiation (1.54 Å) and a liquid N₂ cooled solid-state detector. Thermal analysis, differential calorimetric analysis (DSC), differential thermal analysis (DTA), and thermogravimetric analysis (TGA) were performed on Perkin-Elmer Pyris DSC-1, DTA-7, and Pyris TGA-1 instruments, respectively. Removal of organic species from our samples was confirmed by infrared spectroscopy, obtained with a Perkin-Elmer Spectrum RX FT-IR spectrometer. Flame emission analysis (Perkin-Elmer AAnalyst 100, acetylene/air flame) found <0.5 atomic % Na and K in our Mo₂C and WC samples; however, it is unclear whether the impurities are surface bound or included.

Surface area measurements were made on a custom (in-house) built adsorption apparatus using the BET method with N₂ as the absorption gas and the sample immersed in a liquid N₂ bath. The system is based on classical designs and uses two burets with 11 Hg-filled bulbs to vary total volume.

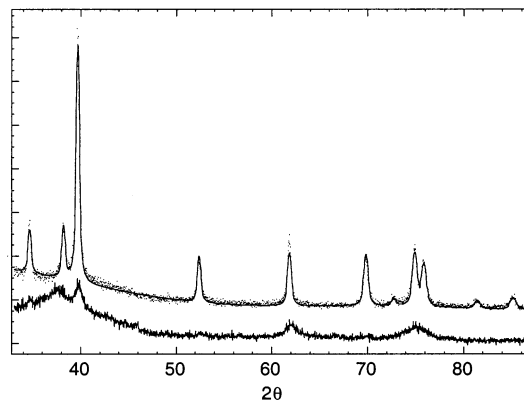


Figure 1. XRD diffraction patterns of Mo₂C annealed briefly to 600 °C (lower, solid line) and for 9 h (upper, dots). The solid line through the upper data is fit.

Pressure was measured with a MKS Instruments 870B capacitance manometer using a 660-B10 power supply/display. The vapor pressure of N₂ at adsorption temperature (P_0) was measured directly with a second Hg manometer. Samples were degassed for 4 h at 400 °C under vacuum (10⁻⁶ Torr) prior to adsorption measurements.

Magnetic characterization was performed with a Quantum Design model MPMS magnetic property measurement system with magnetic quench option (SQUID magnetometer). Samples were vacuum-sealed (10⁻⁶ Torr) in high field NMR tubes and placed butt to butt with an empty, vacuum-sealed NMR tube in a sample straw to minimize background diamagnetism.

Results and Discussion

Mo₂C Synthesis. The product of subambient synthesis, following washing, gives only broad powder X-ray diffraction patterns and diffuse selected area electron diffraction (SAD) patterns, suggesting the material is either amorphous or sub-nanocrystalline. Annealing the material at 600 °C yields a clearly crystalline phase by powder X-ray diffraction. Further annealing of the sample sharpens the pattern and confirms the presence of crystalline Mo₂C (Figure 1). We failed to observe a thermal event in our DSC studies of the annealing process. In addition, no weight change was noted by TGA. Thus, it appears that the transformation from our unannealed X-ray amorphous material to X-ray crystalline Mo₂C is second order in nature. It seems most likely that we are merely crystallizing the particles with little mass transport.

Differentiating α -Mo₂C (orthorhombic, alternatively β' -Mo₂C)²² from β -Mo₂C (hexagonal, L_{3'} structure) phases is extremely difficult by powder X-ray diffraction as the splitting of the reflections is normally, as is the case with our patterns, obscured by the breadth of the peaks. One might assume that the material synthesized a low temperature would be α -Mo₂C, the low-temperature thermodynamic phase that is known to transform to β -Mo₂C at 1190 ± 25 °C. However, it is also known that β -Mo₂C can be quenched in when the carbon content is slightly substoichiometric, i.e., when the composition falls below MoC_{0.50}.²³ Fortunately, the two phases can be easily distinguished by their superconducting critical

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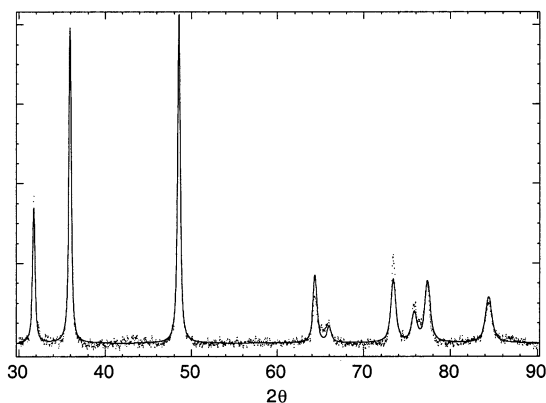


Figure 2. XRD diffraction pattern of WC nanoparticles (dots) with fit (solid line).

temperatures (T_c).²⁴ We measured T_c by observation of the Meissner effect by SQUID magnetometry, finding a value of approximately 12.5 K, consistent with $\alpha\text{-Mo}_2\text{C}$ ($T_c = 12.2$ K)²⁵ and not $\beta\text{-Mo}_2\text{C}$ ($T_c = 2.76$ K).²⁶ Furthermore, the results are consistent with a fully carbidized phase as low carbon stoichiometry has been shown to significantly decrease T_c .

WC Synthesis. The product of subambient synthesis of WC, like that of $\alpha\text{-Mo}_2\text{C}$, was found to yield only broad X-ray diffraction and diffuse SAD patterns indicative of amorphous material. Annealing at 950 °C resulted in a mixture of crystalline WC and $\alpha\text{-W}_2\text{C}$ phases. The coexistence of these two phases is not completely surprising; the WC structure is a line compound at the stoichiometric composition, small C deficiency or perhaps nanoinhomogeneity, in a portion of the nanoparticles might result in the observed mixture. Heating above 1100 °C resulted in the single phase hexagonal $\alpha\text{-WC}$ (Figure 2). Further studies are underway to determine whether the initially mixed phase product is the result of inhomogeneous (insufficiently rapid) mixing during the reduction step.

Surface Area and Morphology. The surface area, determined by N_2 adsorption using the BET method, of our nanoscale crystalline $\alpha\text{-Mo}_2\text{C}$ annealed at 600 °C was found to be 229 m^2/g . TEM micrographs (Figure 3) found these samples to consist of particles having an average diameter of 3.1 nm (Figure 4) with a fairly narrow distribution that is reasonably well described as log-normal.

$\alpha\text{-WC}$, prepared by annealing at 1100 °C, was found to have a surface area of 140 m^2/g . Predictably, particle size was significantly larger and the size distribution much broader for the WC than for $\alpha\text{-Mo}_2\text{C}$; particles as large as ~50 nm were observed mixed in among particles that range in size down to $a \sim 3$ nm (Figure 5).

Conclusions

Surface areas achievable by the synthesis of $\alpha\text{-Mo}_2\text{C}$ and $\alpha\text{-WC}$ nanoparticles by alkali reduction compare

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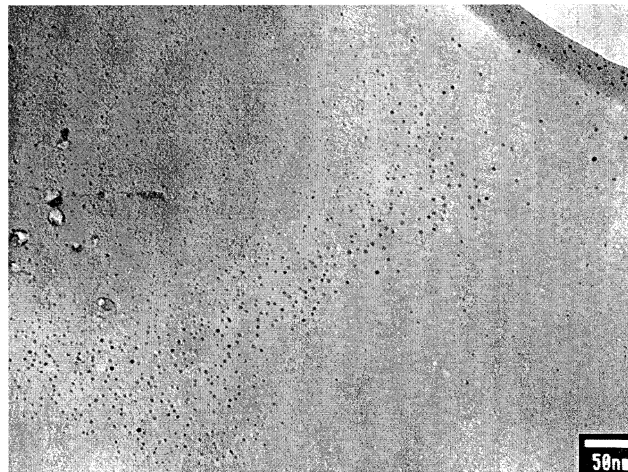


Figure 3. TEM micrograph of $\alpha\text{-Mo}_2\text{C}$ nanoparticles annealed briefly at 600 °C.

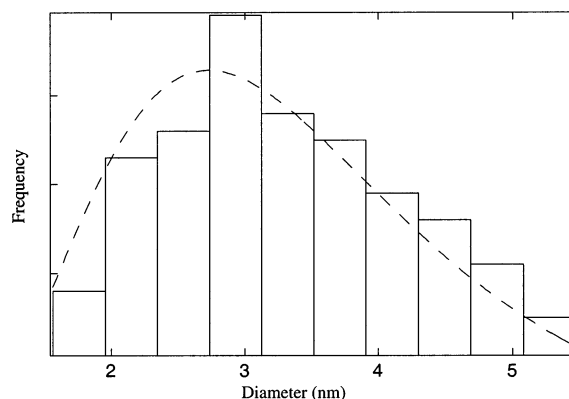


Figure 4. Histogram of $\alpha\text{-Mo}_2\text{C}$ particle diameters measured from TEM micrographs (200 particles). Dashed line is a least-squares fit of the data to a log-normal distribution.

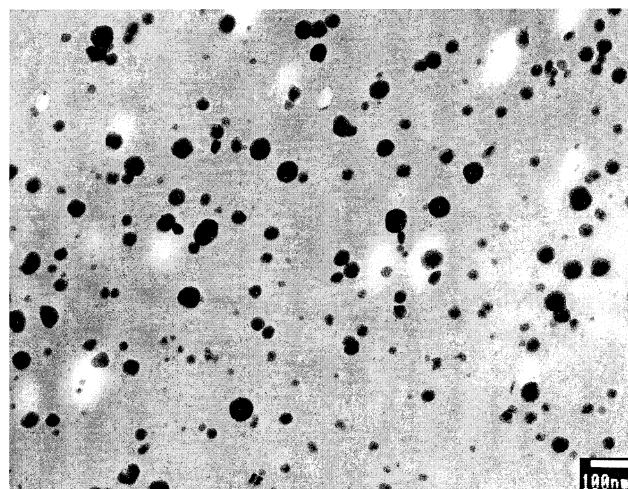


Figure 5. TEM micrograph of $\alpha\text{-WC}$ nanoparticles annealed at 1100 °C.

favorably with the highest achieved by other methods. In fact, alkali reduction is one of only a handful of methods shown to produce these materials with such high surface areas. However, it should be noted that other researchers have found that the catalytic activity of carbides is highly dependent on the details of the synthetic method, presumably due to differences in the surface composition and structure. In addition, it would

be desirable to disperse the catalytic particles on a high surface area support in application. We are currently investigating the catalytic properties of our materials and the synthesis of the carbides on supports.

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