

# High Surface Area Nanoparticulate Transition Metal Carbides Prepared by Alkalide Reduction

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$\text{Fe}_3\text{C}$ , VC, TaC, and TiC nanocrystals have been synthesized by subambient alkalide reduction. The initial products in all cases appear to be either amorphous or sub-nanocrystalline. Annealing between 950 and 1200 °C, depending on the compound, resulted in nanocrystalline materials. Surface areas, measured by the BET method, range between 66 and 164  $\text{m}^2/\text{g}$  and crystallite sizes between  $\sim 2$  and 25 nm.

## 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.<sup>1</sup> 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.

Traditionally, transition metal carbides have been made by high-temperature powder metallurgical techniques, which is energy-intensive and results in large ( $\mu\text{m}$ ) grains of low specific surface area.<sup>2,3</sup> Generally, they are commercially manufactured by reduction of the respective transition metal oxide by carbon at temperatures exceeding 1500 °C, 2000 °C if high phase purity is desired. Methods that achieve high surface area, preferably at reduced processing temperature, are necessary for carbides to fulfill their promise in ceramic and catalytic applications. This technological need has led to considerable interest in methods that are capable of the synthesis of high surface area ( $>20 \text{ m}^2/\text{g}$ ) transition metal carbides.

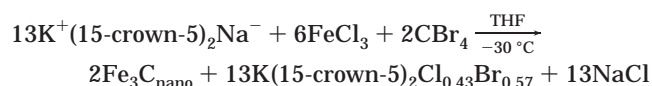
Alkalides are crystalline ionic salts consisting of crown ether or cryptand complexed alkali metal cations charged-balanced by a stoichiometric number of alkali metal anions.<sup>4,5</sup> Alkalides produce alkali metal anions

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 ( $\sim 2$ –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.<sup>6–10</sup>

Previously, we reported that alkalide reduction is capable of producing high surface area  $\alpha$ - $\text{Mo}_2\text{C}$  and  $\alpha$ -WC by co-reduction of the respective metal cation and  $\text{CBr}_4$ .<sup>11</sup> Here, we extend that study and explore the generality of the method for binary carbide synthesis, showing that it is capable of producing nanocrystalline, high surface area  $\text{Fe}_3\text{C}$ , VC, TaC, and TiC.

## Experimental Section

The nanoscale carbides were synthesized by homogeneous alkalide reduction according to the following scheme:



Note the assignment of the  $\text{Br}^-$  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. Anhydrous  $\text{FeCl}_3$  (98%),  $\text{VCl}_3$  (99.99%),  $\text{TaCl}_5$  (99.99%),  $\text{TiBr}_4$  (99.99%), and  $\text{CBr}_4$  (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. Tetrahydrofuran (THF, 99.9+% HPLC-

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grade, inhibitor-free) was purified by stirring over KNa alloy until a persistent blue solution was obtained.  $\text{NH}_3$  (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  $\text{N}_2$ -filled drybox ( $<1$  ppm  $\text{H}_2\text{O}$  and  $\text{O}_2$ ) 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).

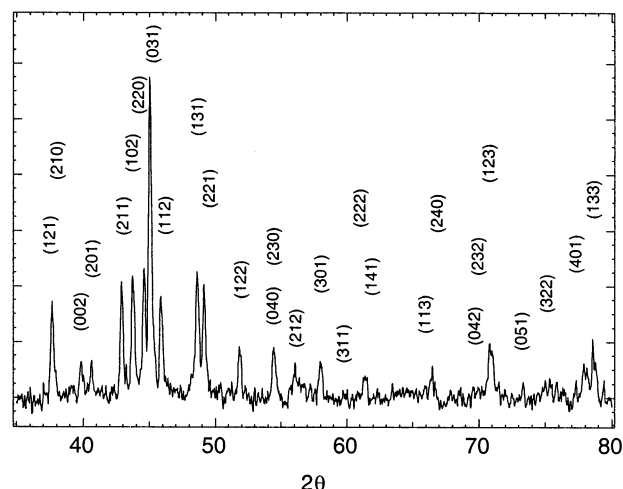
Reactions were carried out in borosilicate H cells<sup>9,12</sup> with coarse frits, modified by replacing one of the stopcocks with an O-ring seal joint, sealed by a mating borosilicate cap and pinch clamp. This modification simplifies reagent loading and product recovery. In a typical reaction, the metal salt and  $\text{CBr}_4$ , in stoichiometric quantity to yield between 0.10 and 0.13 g of the final product assuming 100% yield, were added to the modified side of the H cell. Enough KNa alloy and 15-crown-5 to produce a 5% excess of  $\text{K}^+(15\text{-crown-5})_2\text{Na}^-$  were added to the other chamber of the H cell. Following loading, the cell was immediately cooled to  $-80^\circ\text{C}$  and evacuated to  $<2 \times 10^{-5}$  Torr. Between 20 and 30 mL of THF was added to each side by vacuum distillation. The alkalide solution is formed by complexation of  $\text{K}^+$  by the crown ether dissolved in the THF, with consequent solvation of  $\text{Na}^-$ . Raising the cell temperature to  $8^\circ\text{C}$  melts the KNa alloy, greatly increasing the speed of complexation and enhancing metal salt solubility without incurring significant decomposition. After dissolution of each side ( $\sim 25\text{--}30$  min), the alkalide solution was poured through the frit with simultaneous stirring, immediately reducing the metal salt and  $\text{CBr}_4$ , forming a black powder. The temperature of the cell was then maintained at  $-80^\circ\text{C}$  and generally left overnight to allow the product to fall out of solution. The solvent and excess alkalide was removed by decanting through the frit. Washing several times each at  $-40^\circ\text{C}$  with  $\sim 20$  mL of THF and then liquid  $\text{NH}_3$  was done by distilling the solvent onto the product, agitating, and then removing by decanting. Yield of the reduction should be 100% given the overwhelming reduction potential of  $\text{Na}^-$ ; however, in our small-scale synthesis, some material was lost in recovery, especially in the decanting stages, so actual yields were somewhat less, generally 90–95%. Further synthetic details can be found elsewhere.<sup>6–13</sup>

Electron micrographs were obtained on a JEM-1200EX transmission electron microscope (TEM) operating at 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  $\text{Cu K}\alpha$  radiation (1.54 Å) and a liquid- $\text{N}_2$ -cooled solid-state detector. Removal of organic species from our samples was confirmed by infrared spectroscopy, obtained with a Perkin-Elmer Spectrum RX FT-IR spectrometer.

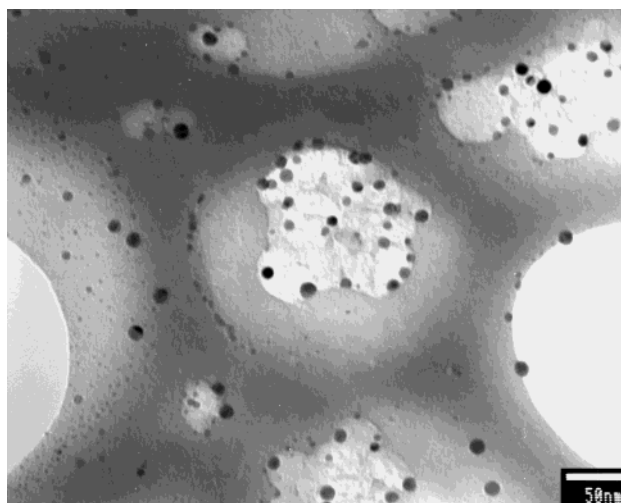
Surface area measurements were made on a custom (in-house) built adsorption apparatus using the BET method with  $\text{N}_2$  as the absorption gas and the sample immersed in a liquid  $\text{N}_2$  bath. The system is based on classical designs and uses two burets with 11 Hg-filled bulbs to vary total volume. Pressure was measured with a MKS Instruments 870B capacitance manometer using a 660-B10 power supply/display. The vapor pressure of  $\text{N}_2$  at adsorption temperature ( $P_0$ ) was measured directly with a second Hg manometer. Samples were degassed for 4 h at  $400^\circ\text{C}$  under vacuum ( $10^{-6}$  Torr) prior to adsorption measurements.

## Results and Discussion

The products of subambient synthesis, following washing, are black, free-flowing particles. The materials give only broad powder X-ray diffraction (XRD) patterns and diffuse selected area electron diffraction (SAD) patterns, suggesting the materials are either amorphous



**Figure 1.** Powder diffraction pattern of  $\text{Fe}_3\text{C}$  nanocrystals annealed at  $950^\circ\text{C}$ . Miller indices are indicated above the reflections.



**Figure 2.** TEM micrograph of  $\text{Fe}_3\text{C}$  nanocrystals annealed at  $950^\circ\text{C}$ .

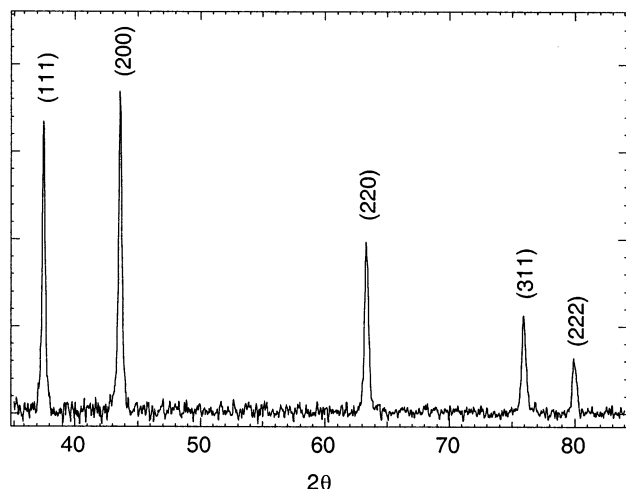
or sub-nanocrystalline. The sizes observed (2–6 nm diameter) are similar to those seen for metal nanoparticles produced by alkalide reduction; however, the particles, while spheroids, are much more irregular. The particles are generally easily dispersed prior to heating, although some loose aggregates can be seen in the micrographs. Following annealing in a vacuum, the morphology of the particles changes as detailed below and crystalline XRD and SAD patterns are obtained in each case.

**$\text{Fe}_3\text{C}$ .** Annealing the product at  $950^\circ\text{C}$  for 4 h yielded nanocrystalline material. X-ray powder patterns show it to be orthorhombic  $\text{Fe}_3\text{C}$ , matching JCPDS PDF #77-0255, as shown in Figure 1. The crystallite size, determined by X-ray peak broadening, was found to be 25 nm. TEM images show that the nanocrystals are well-formed spheroids (Figure 2) that are easily dispersed. Very few particles have diameters as large as 25 nm, the vast majority being between 2 and 15 nm. The surface area of the material was found to be  $123 \text{ m}^2/\text{g}$  by BET gas adsorption measurements.

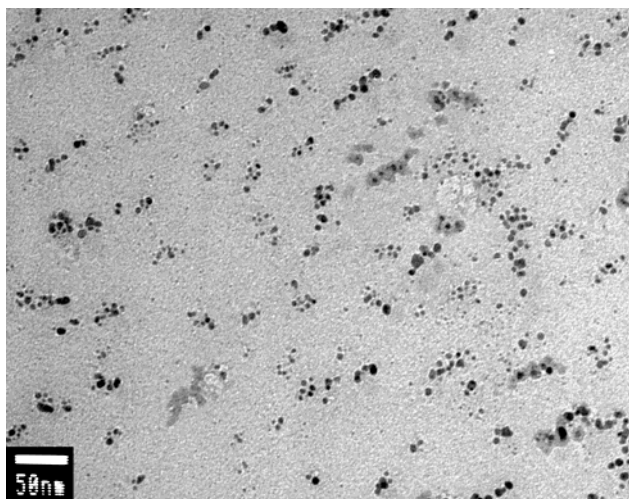
**VC.** Annealing the product at  $1100^\circ\text{C}$  for 1 h yielded nanocrystalline cubic VC (NaCl structure, JCPDS PDF #73-0476), as determined by powder X-ray diffraction

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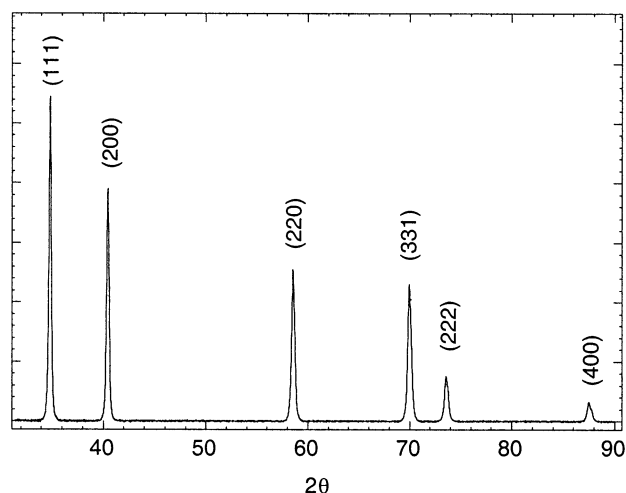
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**Figure 3.** Powder diffraction pattern of VC nanocrystals annealed at 1100 °C. Miller indices are indicated above the reflections.

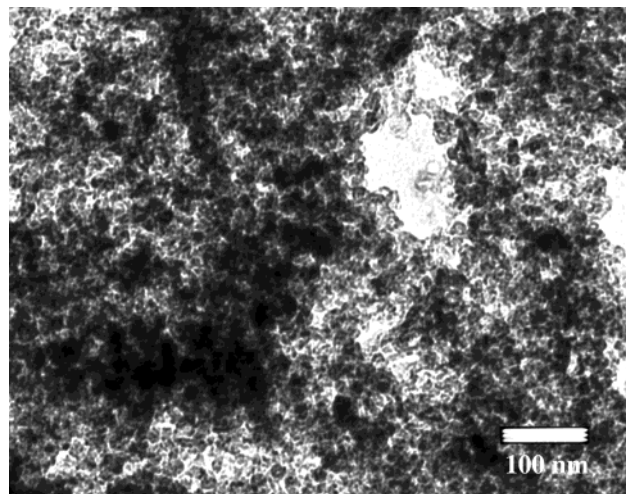


**Figure 4.** TEM micrograph of VC nanocrystals annealed at 1100 °C.

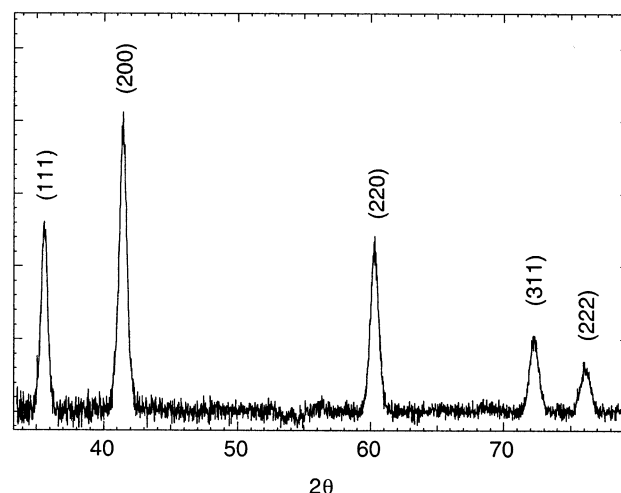


**Figure 5.** Powder diffraction pattern of TaC nanocrystals annealed at 1200 °C. Miller indices are indicated above the reflections.

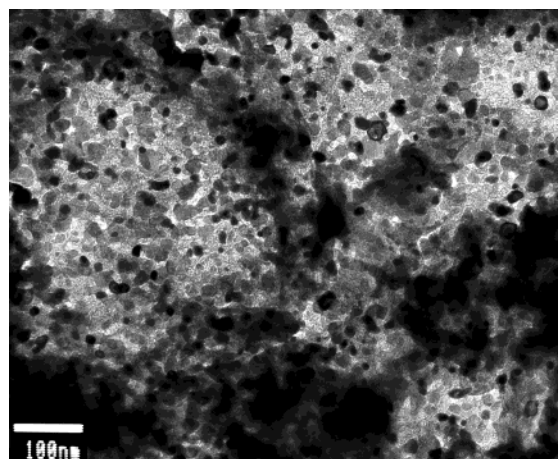
(Figure 3). The average crystallite size, determined from X-ray peak broadening, is 24 nm. The particles are readily dispersed on TEM grids and appear to be roughly spheroidal; many are oblong (Figure 4). As with



**Figure 6.** TEM micrograph of TaC nanocrystals annealed at 1200 °C.



**Figure 7.** Powder diffraction pattern of TiC nanocrystallites annealed at 1100 °C. Miller indices are indicated above the reflections.



**Figure 8.** TEM micrograph of TiC nanocrystals annealed at 1100 °C.

$\text{Fe}_3\text{C}$ , few nanocrystals were observed to be as large as 25 nm, the vast majority being between 4 and 12 nm in their longest dimension. The surface area was found to be 66  $\text{m}^2/\text{g}$ .

**TaC.** Nanocrystals of cubic TaC (NaCl structure, JCPDS PDF #77-0205) result from annealing the prod-



uct at 1200 °C for 1 h (Figure 5). The nanocrystals are of irregular shape and disperse poorly, agglomerating on the TEM grid (Figure 6). The average crystallite size from XRD line broadening is 26 nm; however, the vast majority of particles appear to be between 5 and 22 nm in their largest dimension. Surface area was found to be 110 m<sup>2</sup>/g.

**TiC.** Annealing the product at 1100 °C for 1 h resulted in nanocrystalline cubic TiC (NaCl structure, JCPDS PDF #71-0298) as seen from powder X-ray diffraction (Figure 7). TEM shows the particles to be of highly irregular shape (Figure 8), dispersing very poorly. The average crystallite size from XRD line broadening is 19 nm. It is difficult to assign a range of particle sizes from the micrograph due to the strong agglomeration; however, particles ranging from ~3 to 24 nm are evident. Surface area was found to be 164 m<sup>2</sup>/g.

### Conclusions

Here, we have reported the synthesis of nanocrystalline, high surface area Fe<sub>3</sub>C, VC, TaC, and TiC, and previously  $\alpha$ -Mo<sub>2</sub>C and  $\alpha$ -WC, by alkalide reduction. The general synthetic scheme, that is, the subambient co-reduction of a metal salt and CBr<sub>4</sub> with alkalide

solutions, may well be a general route to nanoscale transition metal carbides.

Surface areas achievable for transition metal carbides synthesized by alkalide reduction are very high and compare favorably with the highest achieved by other methods. The surface areas of  $\alpha$ -Mo<sub>2</sub>C and  $\alpha$ -WC produced by alkalide reduction are as high as any reported.<sup>11</sup> In the case of VC, only one method has been reported that produces higher surface areas than those synthesized by alkalide reduction.<sup>14</sup> The other three carbides reported here, TiC, TaC, and Fe<sub>3</sub>C nanocrystals, have surface areas that are, to the best of our knowledge, the highest ever reported.

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