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

Leroy Covington, Jr, Aruna Shireen Arunagiri, and Kenneth L. Roberts
Department of Mechanical and Chemical Engineering
North Carolina A&T State University, Greensboro, NC

INTRODUCTION:

Interstitial transition-metal compounds, such as molybdenum and tungsten carbide, have found several applications. Because of transition metal carbides great strength and durability, they have traditionally been used at extreme conditions of temperature and pressure. Their hardness has given them applications in cutting tools, golf shoe spikes and snow tires [1].

The carbides of molybdenum and tungsten have been studied extensively for their significant catalytic activity. These compounds have shown great potential for use as commercial catalysts for hydrodenitrogenation (HDN)[2,3].The excellent metal carbides make them desirable as potential nanofiller materials for polymer nanocomposites.

We have used molybdenum trioxide (MoO_3) and tungsten trioxide (WO_3) as parent oxide materials for molybdenum carbide and tungsten carbide syntheses, respectively.

EXPERIMENTAL PROCEDURE:

Temperature Programmed Reaction Synthesis

Powders of molybdenum nitride and molybdenum carbide were synthesized using methods previously reported[4]. Approximately 0.1 g of MoO_3 powder (Aldrich, 99.5+%) was loaded into a stainless steel tube fitted with a porous silica wool and reacted in flowing N_2 (Air Products and Chemicals, Inc, Research Grade) / H_2 (National Welders, Ultra High Purity Grade) or CH_4 (Air Products and Chemicals, Inc., CP Grade) / H_2 at atmospheric pressures, using gas flow procedures and a Barnstead/Thermolyne Tube Furnace (Model F79345) with multi-programmable temperature 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 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.

Figure 1 shows a schematic representation of the reactor/furnace arrangement.

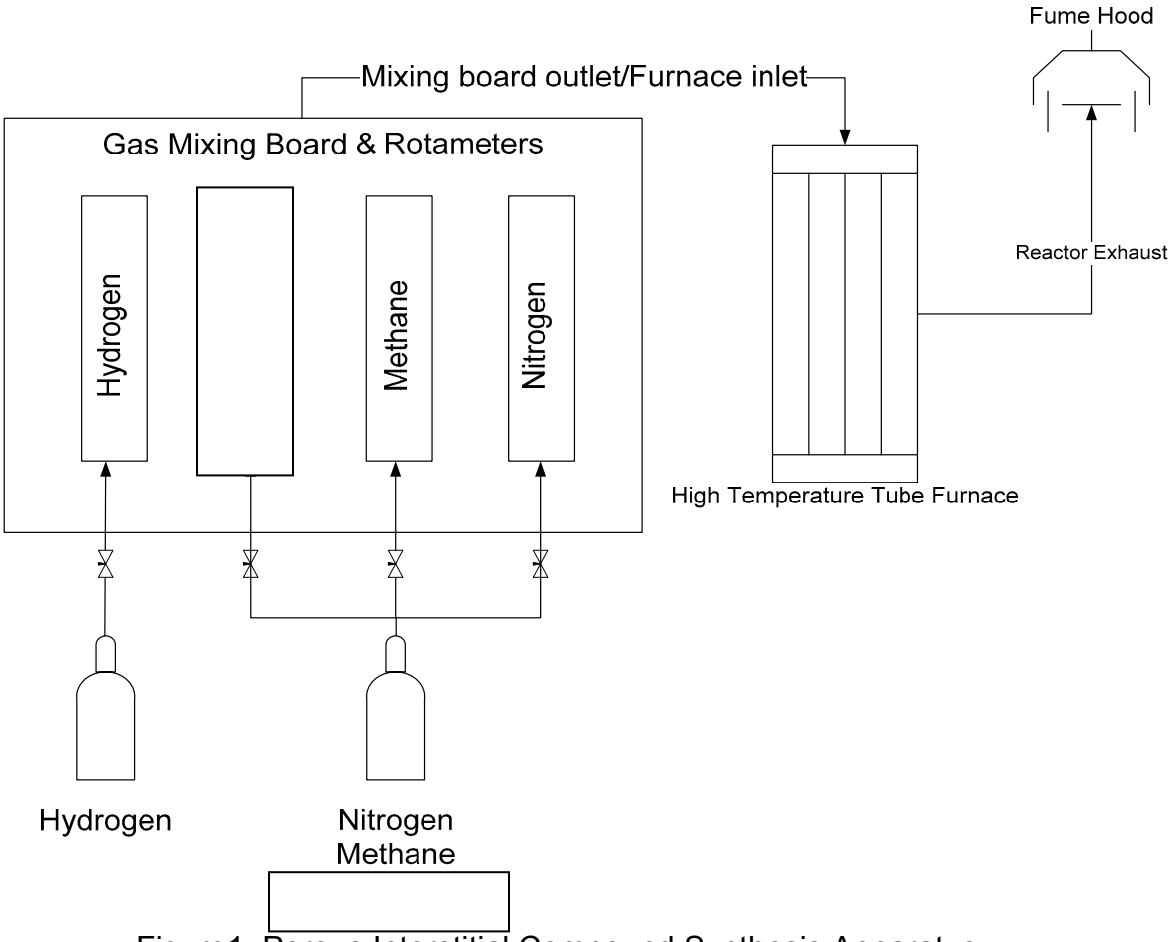

Figure1: Porous Interstitial Compound Synthesis Apparatus

RESULTS:

Molybdenum carbide and tungsten carbide crystallites were synthesized from the reduction and subsequent carburization of the parent oxides, MoO_3 and WO_3, respectively.

Molybdenum Carbide

A series of molybdenum carbides was prepared by the temperature programmed reduction/carburization of MoO_3 with equimolar mixtures of CH_4/H_2. The materials resulting from CH_4/H_2 synthesis were identified through XRD as a hexagonal form of α-Mo_2C.

Observations

These powders were composed of grayish-metallic crystallites. During the preparation of Mo_2C via ultrasonic dispersion an interesting occurrence was noticed. When Mo_2C was contacted with 50 ml of deionized water and sonicated for 15 to 30 minutes to form slurry, the surface of the mixture formed an 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.

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.

Characterization

The identity of molybdenum carbide materials was confirmed using RTXRD measurements. Average crystalline sizes were determined for the ultrasonically dispersed and undispersed molybdenum carbide materials. Surface morphology was evaluated using SEM. Using RTXRD, the only crystalline phase observed in this carbide group was Mo_2C as anticipated since according to the Mo-C phase diagram, only hexagonal Mo2C is thermodynamically stable under the conditions employed in this work.[5] the results were consistent with XRD analysis conducted by Oyama et al. (1988) [6] and Choi et al (1995).[3]. 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. Comparison of the sonicated Mo_2C with the undispersed Mo_2C by means of RTXRD indicated that the bulk phase was Mo_2C. (See figure 2)

The results of scanning electron microscopy on the molybdenum carbide compounds reveal several different surface characteristics. SEM analysis of the Mo_2C was taken at a range interval from 10 microns to 100 nm at magnifications varying from 1, 000 to 40,000. The undispersed Mo_2C at 10 μm and 5,000 magnification, displays a collection of platelets or flake structures on the right hand side. Small resemblances of macrocrystals at the top middle and needle-like crystals along the bottom left side. (See Figure 3). Figure 4 shows dispersed Mo_2C, where there is now an absence of macrocrystals. Flake and needle-like particles appear to be more dispersed in addition; layered thin crystals are present in the upper left corner.

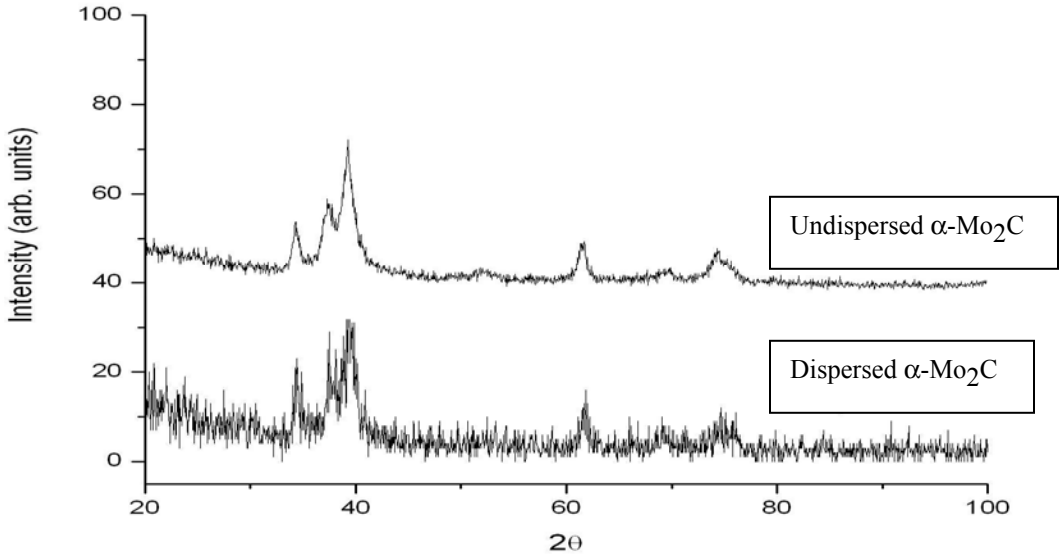

Figure 2: XRD analysis of Undispersed and Dispersed α-Mo_2C nanocrystallites

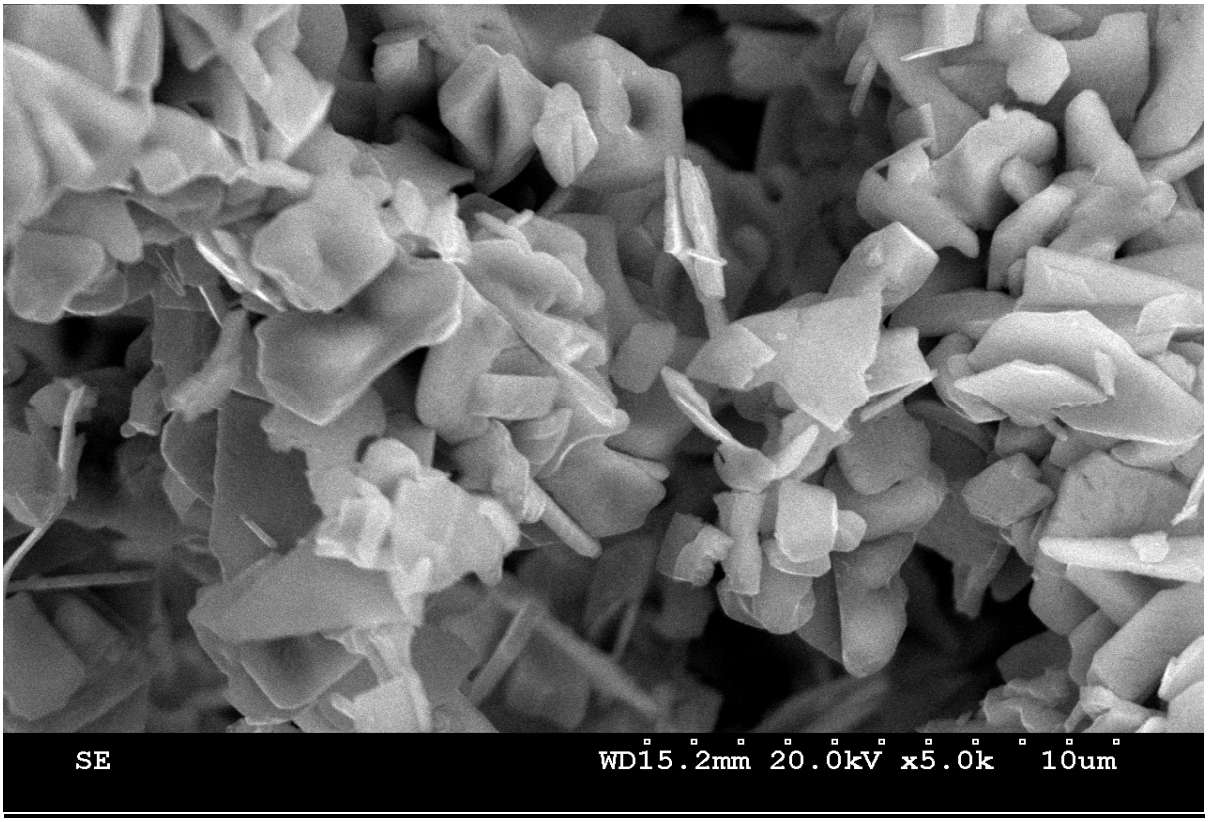

Figure 3: SEM of Undispersed α-Mo_2C at 10 μm Scale and 5,000 Magnification

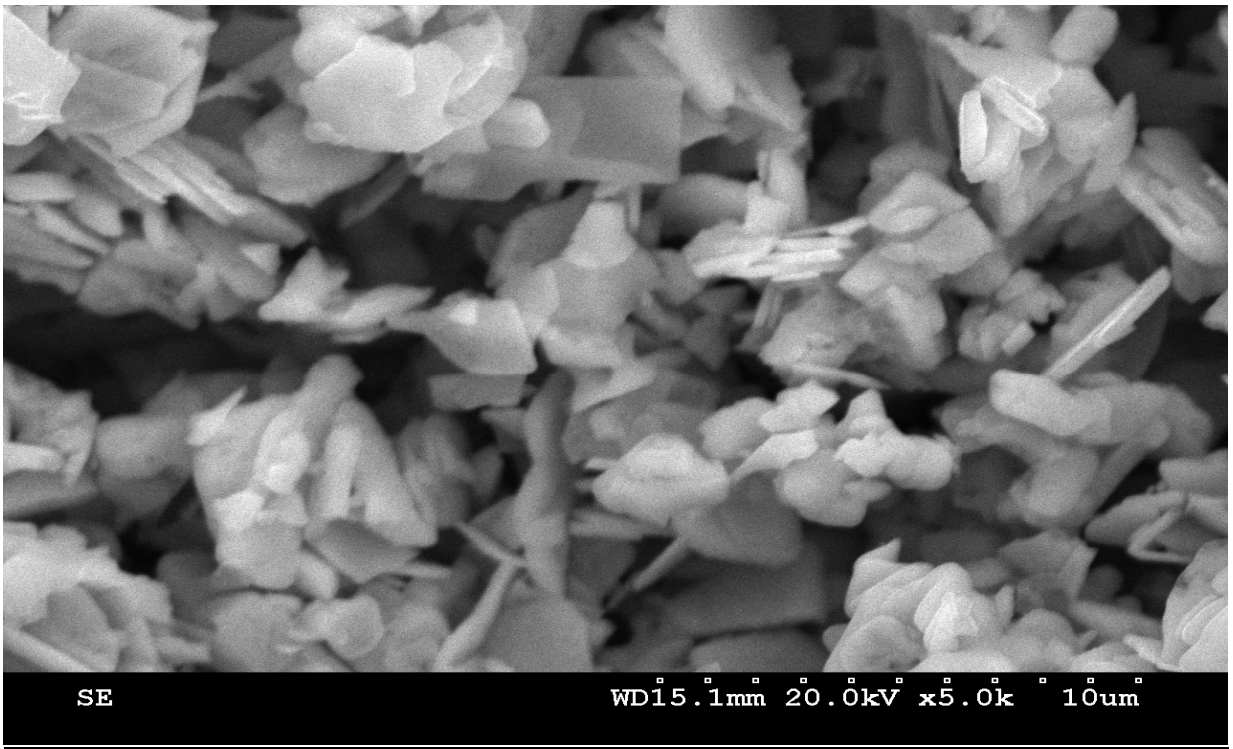

Figure 4: SEM of Dispersed α-Mo_2C at 10 μm Scale and 5,000 Magnification

Tungsten Carbide

A series of tungsten carbides are prepared by the temperature programmed reduction/carburization of WO_3 with equimolar mixture of CH_4/H_2. XRD analyses reveal that body centered-cubic (bcc) tungsten carbide (WC) was produced.

Observations

Upon the addition of deionized water to the tungsten carbide, the solution turned dark gray and an opaque charcoal-like layer formed above the aqueous solution, a result similar to that of Mo_2C. As with the Mo_2C solid-liquid mixture, only rigorous agitation using a touch mixer dispelled the charcoal-like layer into the solution. The jet waves also described during Mo_2C sonication were also observed during the WC dispersion. During the settling period, the solution became clear and light gray in color.

Characterization

XRD was used to confirm the identity as the body-centered cubic tungsten carbide. X-ray reflections found at 35.6°, 48.2° and 31.5° correspond with the (100), (101) and (001) orientation planes, respectively. The crystalline sizes reported in this work are approximately half of those measured by Oyama et al. (1988)[6], the XRD pattern strongly agrees with that presented in the Oyama study. Scherrer analysis of the peak widths shown in figure 5 indicates little change in the size of the crystalline domains.

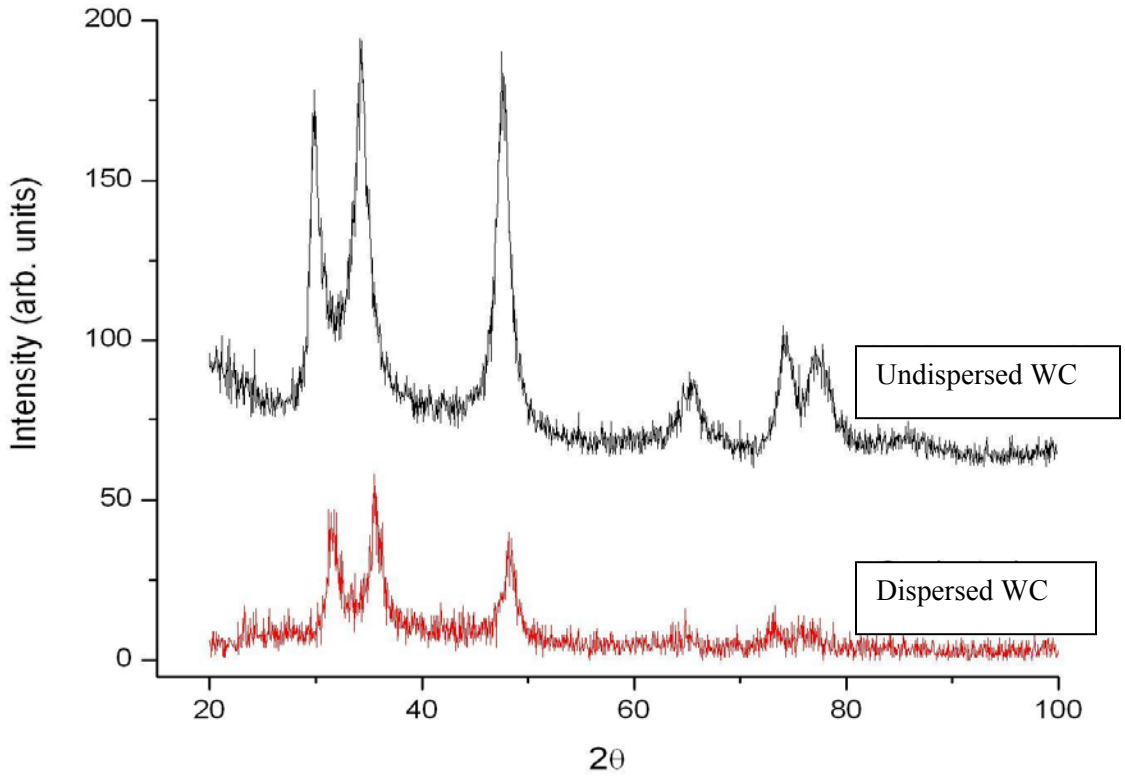

Figure 5: XRD Analysis of Undispersed and Dispersed WC Nanocrystallites

The SEM analyses of the tungsten carbide products show a variety of different surface morphologies. The non-sonicated WC at 10 μm and 5,000 magnification (see Figure 6) shows

undispersed WC as large macrocrystals surrounded by various spherical shaped particles. Figure 7 shows that the large macrocrystals have been dissolved and the spherical particles appear to be agglomerated, with some small particles on the order of approximately 300 nm in size by the use of ultrasonic dispersion.

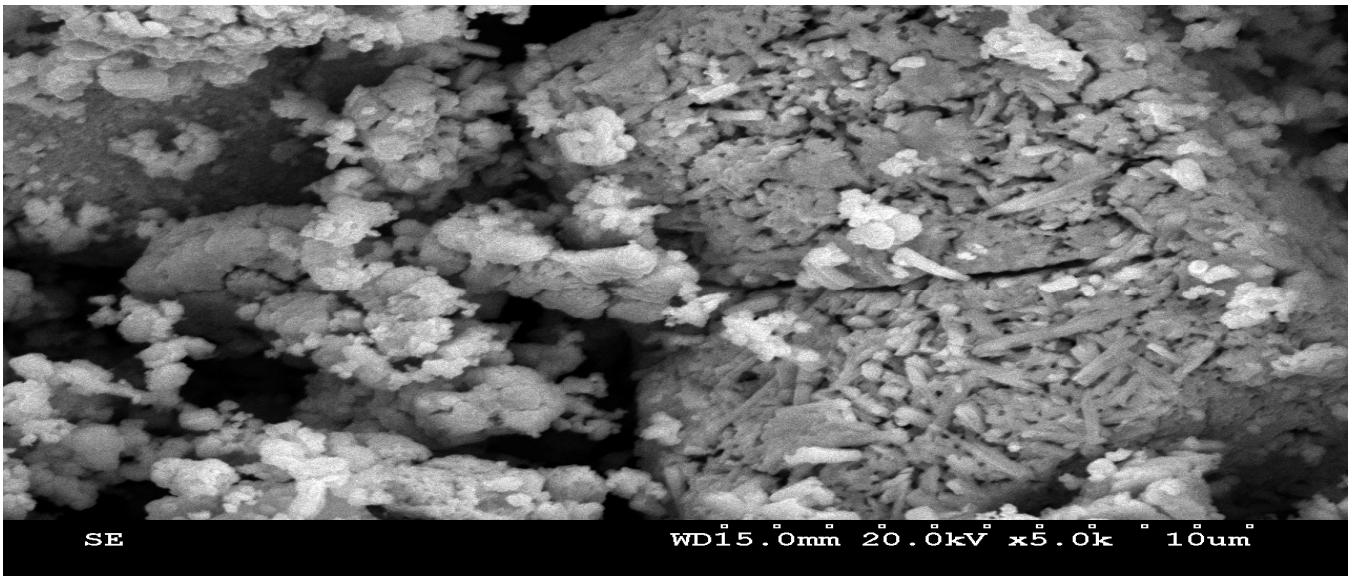

Figure 6: SEM of Undispersed WC at 10 μm Scale and 5,000 Magnification

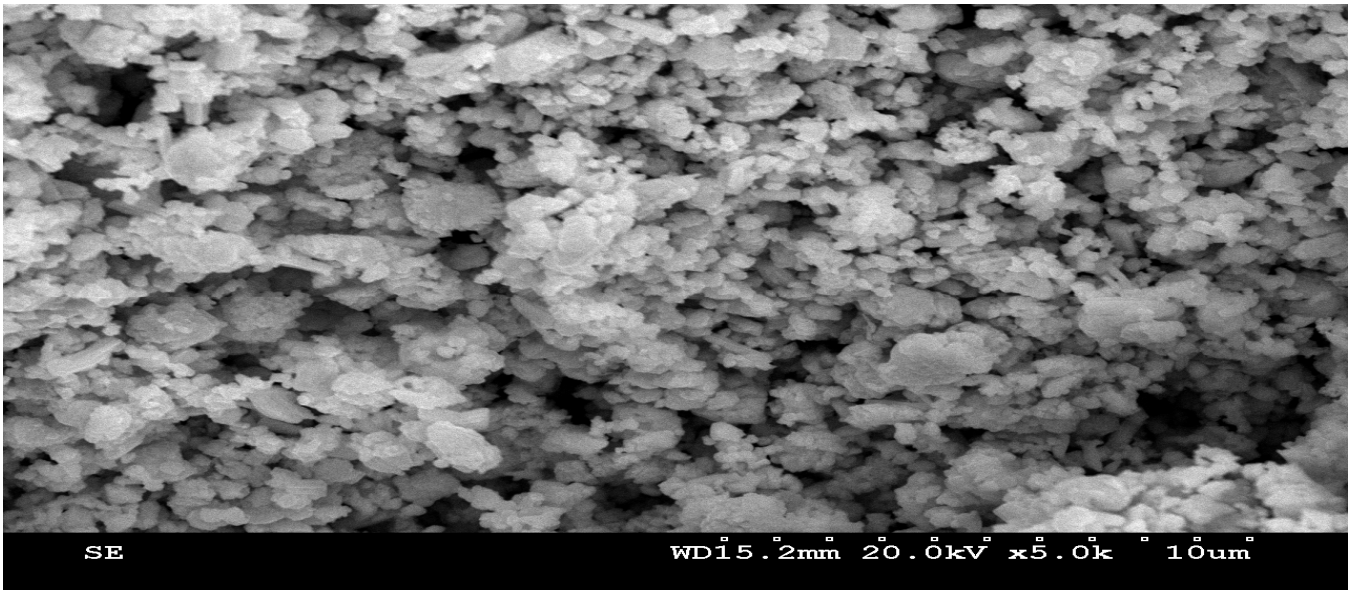

Figure 7: SEM of Dispersed WC at 10 μm Scale and 5,000 Magnification

From the results of XRD and SEM analyses, it was observed that the particles of the ultrasonically dispersed products are polycrystalline agglomerates of a mixture of sub-micron and nanoparticles. For crystalline particles as these, the size of primary nanoparticles can be estimated by the amount by which the x-ray line is broadened, using the XRD information, or determined from the dark-field imaging by TEM or from lattice imaging by high resolution transmission microscopy[7]. The materials produced have melting points of 2520°C and 2870°C, respectively. These values are within the range in which interparticle collision-melting may be experienced[8].

CONCLUSIONS:

Temperature Programmed Reaction (TPR) and ultrasonic irradiation provided an effective pathway to synthesize dispersed transition metal carbide nanocrystallites.

Polycrystalline α-Mo_2C was synthesized from MoO_3 macrocrystals by TPR in CH_4/H_2 gases. The α-Mo_2C crystallites were relatively small and dark metallic-gray in color. Slight changes in temperature ramping rate did not change the structure of the resulting α-Mo_2C.

Body-centered cubic (bcc) WC was prepared by TPR in a CH_4/H_2 reactant gas mixture. Unlike α-Mo_2C synthesis, the WC products were affected by slight changes in the temperature ramping program.

Ultrasonic irradiation provided a convenient route to produce nanoparticles from refractory carbide powders. XRD analyses showed that α-Mo_2C crystallite size was 10 to 14 nm, while the ultrasonically dispersed α-Mo_2C nanomaterials extended slightly to 11 to ~ 15 nm. BCC-WC had an average crystallite size of 9-14 nm and extended slightly to 10-14 nm in the nanomaterials. This work has determined that TPR synthesis of topotactic molybdenum and tungsten carbide powders followed by ultrasonic irradiation can produce transition-metal carbide nanomaterials.

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