Synthesis of Phase Pure Tungsten Carbide for High Temperature H_2 Membranes

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Background

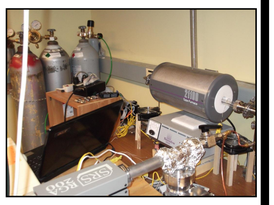
The Pt.-like catalytic behavior of transition metal carbides has been recognized for several decades. However, their potential as robust, highly selective membranes for the steam reforming of methane is only now being realized. The synthesis and properties of molybdenum carbide- are well understood and have been previously studied by this research group. This study aims to apply the body of knowledge gained through previous work with Mo_2C to investigate a new material: tungsten carbide. This paper aims to develop a robust, reproducible procedure for synthesis of phase-pure tungsten carbides.

Motivation

Greater than 95% of the 50 million tons of H_2 produced annually is derived through steam reforming of fossil fuels, which requires energy-intensive separation processes. Membranes offer the potential of significant process simplification and energy reduction, particularly when reforming is combined with the water gas shift reaction and CO_2 capture. Carbide composite membranes offer earth abundant alternatives to Pd.

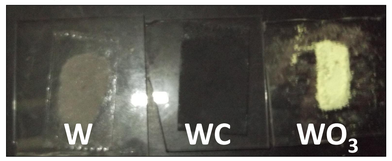
Carburization

1. Procedure adapted from Leclerq et al. (2000).
2. Temperature Programmed Reaction (TPR) set by Thermolyne 21100 tube furnace.
3. Overlaid gas flow regime: 4:1 carburizing CH_4-H_2 mixture.
4. Inert diluent: UHP (5N) N_2.
5. Dwell time: 30 minutes at final temperature.



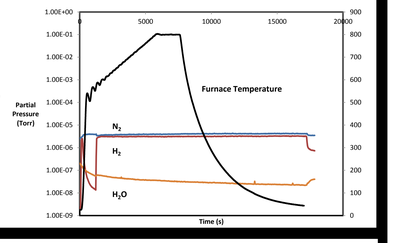
Characterization

1. Bulk crystal structure elucidated using X-Ray Diffraction by Siemens Kristallofex 810 diffractometer.
2. Range analyzed: 20°- 60°.
3. Precision: - Step size: 0.05 °.
   - Count time: 1 s.



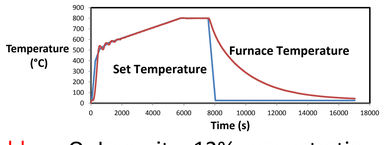
In-situ Residual Gas Analysis (RGA)

- SRS 200 Quadrupole Mass Spectrometer.
- Separates ions based on $\frac{e}{m}$ ratio.
- Analyses partial pressures of exit gas. stream as a function of time.

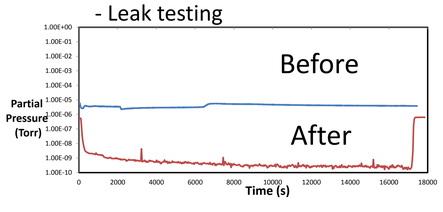


Troubleshooting

1. Problem: Lack of Temperature Control
   Solution: Careful control of ramp rate required. Variation from initial high rate (1.65 °C per s) to lower final rate (0.05 °C per s)



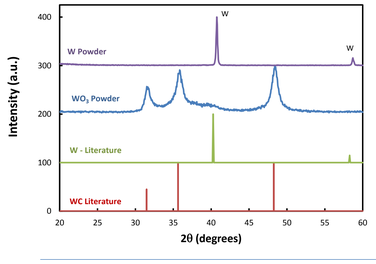
1. Problem: O_2 Impurity- 12% concentration
   Solution: - Replace N2 tank with UHP (5N)
   - Leak testing



Results

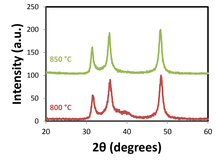
Precursor Comparison

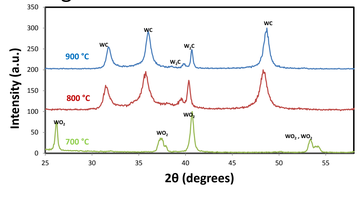
1. Phase pure WC formed from carburization of WO_3.
2. W powder remains un-carburized.
3. 100 mg of each precursor
4. Dwell time: 30 minutes
5. Final temperature: 800 °C



Temperature Series

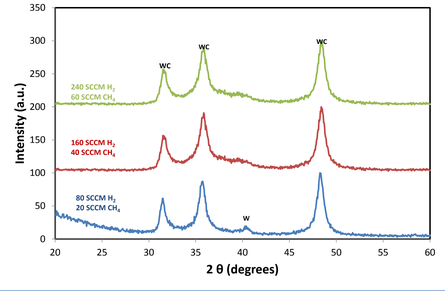
1. Above 800 °C, no increase is noted in the proportion of tungsten mono-carbide.
2. No impetus for increasing temperature above 800 °C.
3. Reduction of WO_2 species is visible between 700 °C and 800 °C.
4. Likewise, α-WC phase emerges.





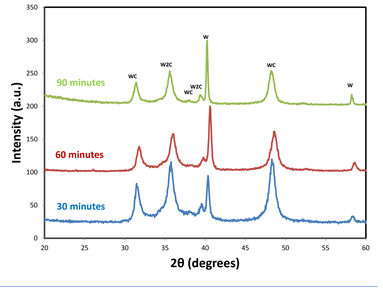
Partial Pressure Series

1. Consistent purephase α-WC produced.
2. W impurity visible at initial lower flowrate (80 SCCM H_2) only.



Dwell Time Series

- Consistent product synthesis.
- Presence of abnormal concentration of O_2 (12%) – non-inert atmosphere.



Film Synthesis

- RF Sputtered WO_x films of intermediate stoichiometry annealed in air furnace for 60 minutes at 450 °C.
- Characterized by XRD to determine initial bulk phase crystal composition.
- Carburized under 4:1 CH_4-H_2 mixture of varying partial pressure, diluted by UHP (5N) purity N_2.
- Film thickness range: 50.1 nm – 86.9 nm
- Characterization inconclusive
- Future work will use PECVD WO_3

Conclusions

1. WO_3 is more conducive to carburization than W metal powder at 800 °C, with a 4: 1 carburizing mixture, with a dwell time of 30 minutes.
2. These conditions are also the optimum experimental conditions for the synthesis of pure bulk phase α-WC.
3. Optimum flow rates: H_2: 160 SCCM, CH_4: 40 SCCM.
4. This project has succeeded in its goal to put in place a reproducible process for the synthesis of bulk phase-pure α-WC powder.
5. Future work will seek to build upon these results in application to thin films. With a reliable for bulk powder synthesis in place it will be possible to synthesize reliable, uniform thin films and to test for H_2 permittivity and selectivity.

Acknowledgements

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Reference: Leclerq et al., 2000. Synthesis of Tungsten Carbides by Temperature-Programmed Reaction with CH4-H2 Mixtures. Influence of the CH4 and Hydrogen Content in the Carburizing Mixture. *J. Solid State Chem, 154,412-426.*