

PRODUCTION OF VERY FINE GRAINED TUNGSTEN CARBIDE POWDERS BY THE $\text{WO}_2(\text{OH})_2$ TRANSPORT REACTION

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INTRODUCTION

The production of very fine grained WC powders is interesting for high performance hardmetal applications because of the positive effects of smaller grain sizes on properties like the hardness of hardmetals ^[1]. However, it is difficult to achieve nanometer grain sizes with traditional processes, which makes it interesting to develop alternatives for the production of these WC powders ^[2-3].

In this study, the chemical vapour transportation (CVT) reaction of WO_3 with H_2O is used to generate gaseous $\text{WO}_2(\text{OH})_2$ ^[4], which directly reacts with a H_2/CH_4 -gas mixture to WC. Due to the reactions in the gas phase, nano-sized WC powder can be obtained. Additionally, it would be a one-step process from WO_3 to WC in contrast to established processes. With the variation of process parameters such as furnace temperature, humidity and gas flows, their effect on the product was investigated and the process further improved.

EXPERIMENTAL

The equipment consisted of two concentric, externally heated quartz tubes. In the smaller tube WO_3 -powder was placed in a quartz boat to generate $\text{WO}_2(\text{OH})_2$ by passing humid argon. This $\text{WO}_2(\text{OH})_2$ flowed into the big quartz tube through a small hole located at the end of the small tube. A mixture of H_2 and CH_4 was lead in the big quartz tube to directly transform the $\text{WO}_2(\text{OH})_2$ into WC. The obtained powders were collected in the colder parts of the outer quartz tube. The products were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM).

RESULTS AND DISCUSSION

In the SEM micrograph (Figure 1), merely agglomerates are visible due to the small crystallite sizes. To specify the crystallite sizes and microstructures TEM investigations were necessary. The grain sizes of the WC powders are in the single-digit nanometer range (about 3-7 nm) (Figure 1). Additionally thin amorphous layers are observed on the particle surfaces, which could be free carbon resulting from the methane decomposition. The electron diffraction pattern (Figure 1) corresponds to the calculated pattern of a NaCl-type (cubic) WC_{1-x} with a lattice parameter of $a = 4,239 \text{ \AA}$ ^[3]. Weaker reflexes indicate small amounts of hexagonal WC. WC_{1-x} is considered as a metastable high temperature modification of WC, which can be stabilized at low grain sizes ^[3, 5].

The X-ray diffraction patterns (Figure 1) of the samples show that beside the hexagonal-WC other phases such as WC_{1-x} , W_2C and W are present. These are formed most likely due to an incomplete carburization reaction. The rare occurrence of oxidic tungsten species in the product indicates that the reduction process is faster than the carburization process.

Additionally, the influences of different process parameters on the product were investigated. Higher Ar-flowrates, higher water concentrations and higher temperatures enhance the transport of $\text{WO}_2(\text{OH})_2$. This increases the yield of powder on one hand, while on the other hand it can result in oxidic tungsten species in the product. The situation is similar with a strong increase of the CH_4 -flow, which results in free carbon in the product. Therefore, it is important to balance the process

parameters, which enhance the transport reaction, with the reducing and carburating agents H_2 and CH_4 .

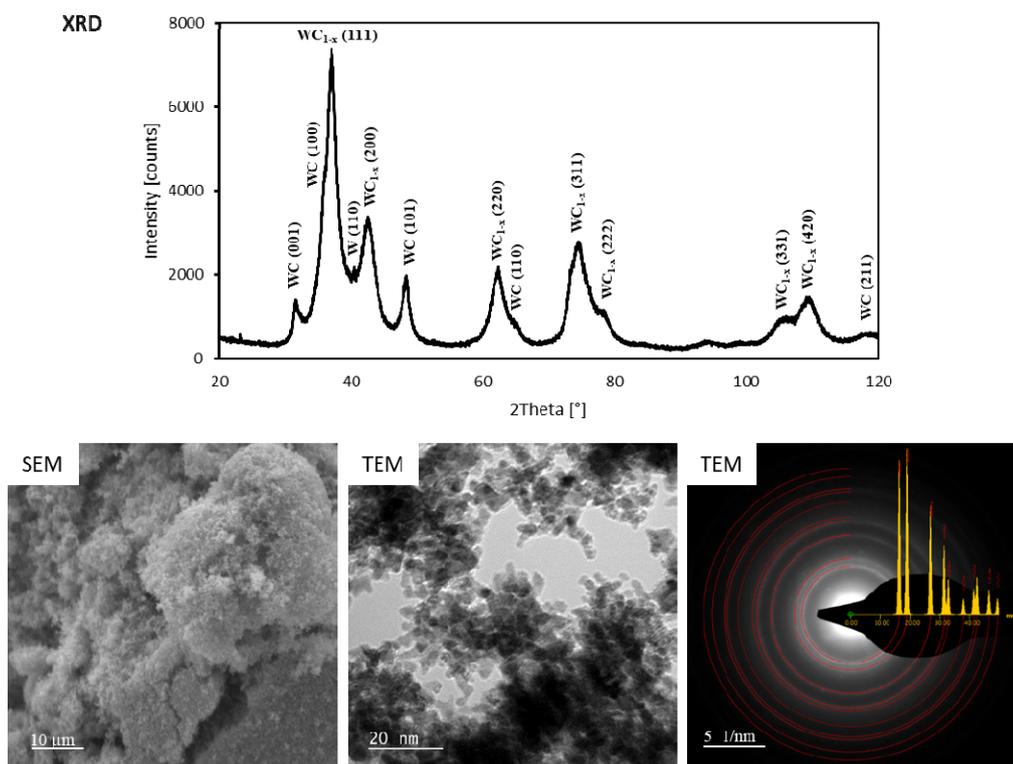


Figure 1: X-Ray diffraction pattern, SEM and TEM micrograph of a produced tungsten carbide powder, measured electron diffraction pattern of the sample with the calculated pattern of WC_{1-x}

CONCLUSION

Using this CVT-based process, the production of tungsten carbide powders with grain sizes in the single-digit nanometer range in a one-step process was achieved. As a result of the small grain sizes a high amount of cubic WC_{1-x} instead of the hexagonal WC is formed. Further characterization will be executed by Raman spectroscopy to investigate the presence of amorphous carbon. The powders could be applied in the hardmetal section and in catalysis as an alternative to noble metal catalysts for example for the conversion of methane to synthesis gas [6].

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