Nanostructured Tungsten Materials by Chemical Methods

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Abstract

Tungsten based-materials are used in many different technical fields, particularly in applications requiring good temperature and/or erosion resistance. Nanostructuring of tungsten alloys and composites has the potential to dramatically improve the materials' properties, enhancing the performance in present applications or enabling totally new possibilities. Nanostructured WC-Co composites have been the focus of researchers and industries for over two decades. New methods for powder fabrication and powder consolidation have been developed. However, the fabrication of true nanograin WC-Co materials is still a challenge. Nanostructured tungsten composites for applications as plasma facing materials in fusion reactors have in recent years attracted a growing interest. This Thesis summarizes work on the development of chemical methods for the fabrication of two different types of nanostructured tungsten based materials; WC-Co materials mainly aimed at cutting tools applications and W-ODS composites with rare earth oxide particles, intended as plasma facing materials in future fusion reactors. The approach has been to prepare powders in two steps: a) synthesis of uniform powder precursors containing ions of tungsten and the doping elements by co-precipitation from aqueous solutions, and b) further processing of the precursors into W or WC based nano-composite powders.

Highly homogenous W and Co containing powder precursors for WC-Co composites were prepared via two different routes. Keggin-based precursors \((\text{NH}_4)_8[H_2\text{Co}_2\text{W}_{11}\text{O}_{40}]\) with agglomerates of sizes up to 50 μm, were made from sodium tungstate or ammonium metatungstate and cobalt acetate. The powder composition corresponded to 5.2 % Co in the final WC-Co composites. In a second approach, paratungstate-based precursors \((\text{Co}_x\text{(NH}_4)_{10-2x}[\text{H}_2\text{W}_{12}\text{O}_{42}])\) were prepared from ammonium paratungstate (APT) and cobalt hydroxide with different compositions corresponding to 3.7 to 9.7 % Co in WC-Co. These particles had a plate-like morphology with sides of 5-20 μm and a thickness of less than 1 μm. Both precursors were processed and sintered into highly uniform microstructures with fine scale (<1 μm). The processing of paratungstate-based precursors was also further investigated. Nanostructured WC-Co powders with grains size of less than 50 nm by decreasing processing temperatures and by applying gas phase carburization.

W-ODS materials were fabricated starting from ammonium paratungstate and rare earth elements (Y or La). Paratungstate-based precursors were prepared with different homogeneity and particle sizes. The degree of the chemical uniformity varied with the particle size from ca 1 to 30 μm. Tungsten trioxide hydrate-based precursors made from APT and yttrium nitrate under acidic conditions had dramatically higher homogeneity and smaller particle size. The crystallite size was decreased to a few nanometers. These precursors were further processed to composite nanopowder and sintered to a nanostructured W-1.2%Y₂O₃ composite with 88% relative density.

In summary, APT can be converted to highly homogenous powder precursors of different compositions. The transformations are carried out in aqueous suspensions as a solvent mediated process, in which the starting material dissolves and the precursor precipitates. Powders with fine scale morphologies are obtained, e.g. plate-like particles with thickness less than 1 μm or spherical particles with size of a few nanometers. These precursors were processed further into nano-sized composite powders and sintered to highly uniform tungsten composites with fine microstructures.
Papers included in the Thesis


III. S. Wahlberg, M. A.Yar and M. Muhammed, Oxide Dispersed Tungsten Powders from Rare Earth Doped Ammonium Paratungstate, in manuscript

IV. S. Wahlberg, M. A. Yar, M. O. Abuelnaga, H.G. Salem, M. Johnsson and M. Muhammed, Fabrication of Nanostructured W-Y2O3 Materials by Chemical Methods, in manuscript

Related Patents


Other publications not included in the thesis


Contributions of the author

Paper I. Part in generation of ideas, performing all synthesis of precursors, writing the article

Paper II Part in generation of ideas, performing all synthesis of precursors and part of processing, writing part of the article

Paper III Generating ideas, performing all experimental work apart from SEM, writing the article.

Paper IV Generating ideas, performing powder fabrication and characterizations apart from SEM and TEM, writing parts of the article
**Abbreviations and symbols**

- **ODS**: Oxide dispersion strengthened
- **SPD**: Severe plastic deformation
- **APT**: Ammonium paratungstate
- **AMT**: Ammonium metatungstate
- **TBO**: Tungsten blue oxide
- **CVT**: Chemical vapor transport
- **MA**: Mechanical alloying
- **HIP**: Hot isostatic pressing
- **TTH**: Tungsten trioxide hydrate
- **SPS**: Spark plasma sintering
- **ICP**: Inductively coupled plasma
- **XRD**: X-ray diffraction
- **SEM**: Scanning electron microscope
- **EDX**: Energy-dispersive X-ray spectroscopy
- **TEM**: Transmission electron microscope
- **TGA**: Thermal gravimetric analysis
- **FTIR**: Fourier Transform Infrared Spectroscopy
- **EGA**: Evolved gas analysis
- **Hv50**: Hardness
- **Kt**: Fracture toughness
- **TG**: Thermogravimetry
- **DTG**: Derivative thermogravimetry
- **BSE**: Back-scattered electrons
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1 Introduction

1.1 Tungsten Materials – Properties and Applications

Tungsten plays a key role in many technical systems. The element has in its pure form unique properties such as high hardness, good thermal and electrical conductivity as well as the highest melting point of all metals. Accordingly it is used in many different applications where good wear resistance and/or high temperature stability are required [1, 2]. Tungsten is, similar to other refractory metals, brittle at room temperature, which is not only a major concern in many applications but also during the fabrication as it makes mechanical processing more difficult. The brittleness is related to the body-centered cubic (bcc) lattice, but at the same time also a function of the microstructure and composition of the material. A decrease of the grain size results in an increased ductility, while impurities such as oxygen and nitrogen can weaken the grain boundaries leading to a more brittle material. The properties of tungsten materials are strongly dependent on the raw materials used, as well as on the method of fabrication, as those factors have a large impact on the material’s microstructure and impurity levels.

The brittleness of the metal is a limiting factor in many applications. Different alloys and composites constitute a major part of the total tungsten consumption. The first commercial use of tungsten was as alloying element in steels during the 19th century. Production of tungsten filaments for incandescent lamps started in the beginning of the 20th century. The filaments were at start made from pure tungsten and very brittle. More ductile tungsten filaments were achieved by the addition of a small amounts (1-2 wt%) of ThO₂ particles to the tungsten matrix. The resulting oxide dispersion strengthened (ODS) composite showed improved stability at high temperatures. The oxide particles impede the mobility of grain boundaries, leading to finer a microstructure after sintering as well as an increased recrystallization temperature. Further improvement of the incandescent filaments was made with another approach using K-Na-silicate doping, so-called non-saging tungsten [3]. Cemented carbides, with cobalt as binders (WC-Co) were introduced on the market during the 1920s. The composite combines the hardness and wear resistance of the carbide with the toughness of the ductile cobalt binder. The mechanical properties of cemented carbides can be tailored for different applications by varying the carbide grain size (< 30 μm) or the cobalt content (3-30 wt%). In general, the hardness of the material increases with decreasing grain size while the toughness increases with the content of the cobalt binder. The materials are used worldwide mostly for metal-cutting and shaping tools, playing a key role for the productivity in many manufacturing industries. Cemented carbide materials constitute more than half of the global tungsten consumption. The second most important use of tungsten is as alloying element in hard, wear resistant high speed steels. These materials are, similar to the cemented carbides, mostly used for tools. Traditional incandescent light bulbs with tungsten based filaments are today only a minor fraction of the global tungsten consumption. They are in many countries being replaced by more modern and less energy consuming lamps, which also may contain tungsten in its different components.

As in other fields, there has also been a growing interest in tungsten-based nanomaterials, solids with grain size in the range of 1 – 100 nm and a large fraction of the atoms in grain boundaries. Often, increased strength and hardness can be observed as the grain size is decreased. Nanostructured WC-Co composites have been in the focus of researchers and industries for
more than two decades, while tungsten-based nanocomposites for applications as plasma facing materials in fusion reactors have started to attract a growing interest in recent years.

1.2 Nanostructured Cemented Carbides

Since the 1980s there has been a shift towards cemented carbides with finer grain size [4, 5]. Composites with submicron (0.5-0.9 μm) or ultrafine (0.2-0.5 μm) grain size are being used in different demanding applications, e.g. for very fine drill tips for the manufacture of miniaturized printed circuit boards (Fig. 1.1). Small amounts (<2 wt%) of grain growth inhibitors like VC or Cr₃C₂ are often added to mitigate the growth of WC grains during the sintering step [5-7]. The main advantages of these materials are the improved performances mainly related to their high hardness combined with high strength. The effect of the grain refinement on the toughness of the materials is less well understood. For conventional WC-Co grades, the toughness is known to increase with the WC grain size. Several reports indicate a different trend as the grain size is decreased towards the nano-regime, materials with high hardness and rather high toughness have been fabricated [6]. Nanostructuring has the potential of dramatically improve the mechanical properties and the performance of materials with high hardness, strength and as well as good toughness. However, the fabrication of WC-Co materials with true a nano-scale (<100 nm) remains a challenge, mainly due to extensive grain growth during sintering of nano-scale powders [6, 8].

1.3 Tungsten-Based Nanocomposites for Fusion Applications

The steady increase of the use of fossil fuels has contributed to an increase of the greenhouse gas carbon dioxide in the atmosphere. The development of sustainable energy sources, free from carbon dioxide emissions, is a major challenge for the future. There has been recent renaissance for the use of fission nuclear energy with a number of new reactors being constructed worldwide. Beside fission technology, fusion nuclear technology is considered as a more safe future alternative with the fuel, deuterium and lithium, available in large quantities [9]. However, a number of technical challenges have to be addressed before the realization of commercial fusion power plants. One of the most critical issues is the selection of materials facing the plasma inside the fusion reactor.

Fig. 1.1, Printed circuit board drill with a tip diameter of 0.25 mm.

Fig. 1.2, Fusion reactor ITER, France (Under construction)

The plasma facing materials in a future fusion reactor must be able to withstand extreme physical conditions including temperatures above 3000°C, sputtering erosion and neutron radiation (Fig. 1.2). Tungsten and tungsten based materials are with their excellent stability at higher temperatures suitable candidates for this application [10]. However, the brittleness of
conventional tungsten grades will be a major limitation risking material’s failure induced by either mechanical loads or thermal shocks. Continued exposure to the reactor environment will also cause further embrittlement due to recrystallization and radiation damage [11-14]. Hence, there is a strong interest in the development of new tungsten materials optimized for use in a fusion reactor. An effective way of improving the strength and ductility is by decreasing the grain size down to the ultrafine or nano-scale, e.g. ultrafine tungsten produced by severe plastic deformation (SPD) has shown significantly improved fracture toughness as compared to conventional micron-sized grades [15]. Another aspect is the stability of the microstructure towards grain growth (recrystallization) at elevated temperatures. The mobility of the grain boundaries can be hindered by the addition fine particles of a second stable phase [16], as in the case of W-ODS filaments mentioned above. Nanostructuring may also be a way improving the material’s resistance to radiation damage, with short distances to grain boundaries which can act as sinks for defects induced during irradiation [16, 17]. Promising candidates are nanostructured ODS composites with La2O3 [11] or Y2O3 particles in the tungsten matrix. Another alternative is the use TiC as the stabilizing phase [18, 19].

1.4 Fabrication of Conventional Tungsten Materials

The main part (70-80 %) of all tungsten materials are produced via powder metallurgy. The approach offers flexibility and possibilities to control both the composition and the microstructure of the final material. The process can be divided in different steps starting by the extraction of the element from the ore, followed a number of operations such as reductive decomposition under hydrogen, blending with other components, sintering and different post-treatments (Fig. 1.3) [1, 2]. Each step may influence the materials’ characteristics such as homogeneity, grain size and/or impurity levels and therefore also the properties of the final materials.

![Flowchart showing the process of conventional tungsten fabrication](Fig. 1.3, Powder metallurgical processing of conventional tungsten based materials)

1.4.1 Fabrication of Ammonium Paratungstate (APT) Powders

Tungsten is extracted from the ore and converted to the highly pure intermediate product ammonium paratungstate (APT) by hydrometallurgical methods, i.e. processing based on aqueous solution chemistry. Ores containing tungsten as scheelite (CaWO4) or wolframite ((Mn, Fe)WO4) are crushed and enriched by flotation technique to ore concentrates containing 10-75 % WO3. These raw materials are first calcined in oxidizing atmosphere at 500-600°C to remove surfactants added to facilitate the flotation process. Wolframite concentrates are leached in
NaOH solutions, while scheelite, stable in sodium hydroxide solutions [20] is treated by Na₂CO₃ solutions. The obtained Na₂WO₄ solutions are further purified by a number of precipitation reactions to remove elements like Si, P, F and Mo. The next step is the exchange of sodium for ammonium in a solvent extraction or ion exchange step. The resulting ammonium tungstate solution is then heated to evaporate water and ammonia, increasing the tungstate concentration as well as decreasing the pH of the solution. Paratungstate ions are formed and crystallize with ammonium as APT (Eq. 1.1).

\[
10 \text{NH}_4^+ + [\text{H}_2\text{W}_{12}\text{O}_{42}]^{10^-} + 4 \text{H}_2\text{O} \rightarrow (\text{NH}_4)_{10}[\text{H}_2\text{W}_{12}\text{O}_{42}] \cdot 4\text{H}_2\text{O} \text{ (s)}
\] (1.1)

An alternative raw material source is tungsten scrap which via oxidation can be converted into sodium tungstate and converted to APT in the same way. An environmental friendly approach which also can save costs since scrap often is rich in tungsten and has low levels of impurities. The purity of a tungsten intermediate such as APT is of major importance since it also limits the purity of the final tungsten material. The level of contaminating elements in tungsten materials has decreased partly as a result of improved hydrometallurgic processing [1]. An important step was the introduction of modern solvent extraction or ion exchange techniques for the conversion of sodium tungstate to ammonium tungstate solutions. APT of high purity is also used as starting materials for the fabrication of other tungsten compounds such as tungstic acid, ammonium metatungstate (AMT), tungsten trioxide (WO₃) and the slightly reduced tungsten blue oxide (TBO), a product which is a actually a mixture of several different tungsten compounds.

1.4.2 Reduction to Tungsten Powders

The reduction step mostly starts from WO₃ or TBO obtained by heating APT at 400-900 °C in air or in slightly reducing atmosphere containing hydrogen or mixtures of hydrogen and nitrogen. Metallic tungsten powders are prepared by the reduction in hydrogen atmosphere at a pressure of 1 atm and temperatures between 600-1100 °C in pusher or rotary furnaces. The overall reaction can be described as in Eq. 1.2.

\[
\text{WO}_{3-x} \text{(s)} + (3-x) \text{H}_2 \text{(g)} \rightleftharpoons \text{W} \text{(s)} + (3-x) \text{H}_2\text{O} \text{(g)}
\] (1.2)

Tungsten trioxide (WO₃), or slightly reduced tungsten oxides (WO₃ₓ), react with hydrogen to produce tungsten metal and water. The conversion of the oxide to metal is known to progress stepwise from WO₃ via WO₂₋₀, WO₂₋₁ and/or WO₂ to W. The actual reaction path varies with several parameters such as temperature, humidity, and the purity of the oxide. Water molecules formed in the reduction are removed by diffusion through the powder and ventilated out from the furnace with the flowing stream of hydrogen. The humidity within the powder bed is mainly a function of its resistance to water transport, determined by the bed’s porosity and height. Also the flow rate of the hydrogen is of importance. The rate of the nucleation of W from WO₂ is strongly dependent on the humidity (Eq. 1.3). The transport of water vapor out from the powder bed is under industrial conditions normally the overall rate determining step of the process.

\[
\text{WO}_2 \text{(s)} + 2 \text{H}_2 \text{(g)} \rightleftharpoons \text{W} \text{(s)} + 2 \text{H}_2\text{O} \text{(g)}
\] (1.3)
The humidity has also a large impact on the formation mechanisms which controls the size and shape of the tungsten grains. Dry conditions and low temperatures favor nucleation and transformation of the oxide to metal in the solid state. The result is a powder consisting of very fine grains, often agglomerated in shapes resembling the original oxide. Another mechanism occurs at higher temperatures and under more humid conditions. In this cases, water plays a role by reacting with tungsten oxide \( \text{WO}_{3-x} \) or tungsten metal particles to form a volatile hydrated tungsten oxide \( \text{WO}_2(\text{OH})_2 \) (Eq. 1.4).

\[
\text{WO}_{3-x} (s) + (1+x) \text{H}_2\text{O} (g) \rightleftharpoons \text{WO}_2(\text{OH})_2 (g) + x \text{H}_2 (g)
\]  

(1.4)

The partial pressure of the gaseous \( \text{WO}_2(\text{OH})_2 \) increases with the \( P_{\text{H}_2\text{O}} \) and the temperature. This molecule can diffuse to, and subsequently be reduced at, a growing tungsten grain (Eq. 1.5).

\[
\text{WO}_2(\text{OH})_2 (g) + 3 \text{H}_2 (g) \rightleftharpoons \text{W} (s) + 4 \text{H}_2\text{O} (g)
\]

(1.5)

The resulting reaction path via chemical vapor transport (CVT) offers an efficient growth mechanism and produces large grains and morphologies different from the starting oxide.

Hence, water vapor plays a central role in several ways during the reduction of tungsten oxides, affecting the reaction rate as well as the morphology of the final powder. The effect of water on the morphology is used industrially to control the grain size. Very fine powders are made under dry conditions at low temperatures with low powder beds and high gas flow rates in order to remove water molecules formed in the process. Coarse powders are made using humid hydrogen gas at higher temperatures to accelerate the growth of the tungsten grains.

### 1.4.3 Fabrication of Tungsten Composite Powders

Next step in the fabrication of tungsten based composites is normally mechanical mixing of the tungsten powder with other components in the form of elements or compounds. The preparation of tungsten carbide powder is made by blending tungsten powder with solid carbon. The two components are milled together to achieve a homogenous distribution of the elements. The mixed powder is then heated at 1300-1700°C under hydrogen atmosphere to react and form tungsten carbide (WC). It is essential to control the stoichiometry of the carburization reaction. Carbon deficit leads to the formation the brittle \( \text{W}_2\text{C} \), while a surplus would result in residues of free carbon which also has a negative effect on the mechanical properties of the final material. The mechanical mixing step makes it easy to control the amounts of the different components.

In the fabrication of WC-Co composites, cobalt powder is milled together with the WC powder. Other components such as organic solvents and lubricants can also be added at this point. The purpose of the WC-Co milling step is to deagglomerate the powders but also to achieve a uniform mixing of the different components. The mixture after milling is spray-dried to remove the organic solvent producing granules of WC, Co and organic lubricants.

Other types of composites can also be made in a similar way. Tungsten powders are milled with fine powders of \( \text{ThO}_2 \) or \( \text{La}_2\text{O}_3 \) to uniform mixtures of W with \( \text{ThO}_2 \) or \( \text{La}_2\text{O}_3 \).
1.4.4 Sintering and Post Treatments

The obtained powders are pressed and sintered to solid composite materials. WC-Co materials are sintering at temperatures up to 1600 °C depending on the grain size and amount of cobalt. Different post treatments such as coating or machining are common. Sintering of W-ThO₂ materials are carried out at temperature up to 2800°C. The obtained materials can be worked mechanically to increase densities and improve the mechanical properties.

1.5 Fabrication of Ultrafine and Nanostructured Tungsten Composite Materials

Critical parameters affecting the properties of powders are mainly particle size and particle size distribution. The degree of agglomeration is an important factor. The scale of the microstructures is often related to the size of powder agglomerates before sintering [21]. Another aspect is the presence of impurities, either from the starting materials or introduced during the process, able to significantly deteriorate the material’s properties by e.g. causing substantial grain growth, weakening of grain boundaries or by the formation of additional undesirable phases. Conventional tungsten composites are made with grain size down to the submicron range. Mechanical mixing and milling of powders limits the chemical homogeneity and the microstructural scale to the size of the milled powders [22]. The milling step also results in contamination by the wear of the milling equipment and media [23]. Further decrease of the material’s microstructure to ultrafine or nano-scale requires high quality raw materials and refined or totally different and innovative fabrication techniques.

Nanostructured composite powders can be fabricated in several different ways. A commonly used method is mechanical alloying (MA), a top-down approach in which micron sized particulates are extensively milled and fractured to the nano-regime. One purpose is to decrease the grain size of the starting powder. Another aim is to achieve a high degree of mixing of the different components. The method has been exploited for fabrication of WC-Co powders [6] as well as for W-TiC powders for ultrafine dispersion strengthened composites for fusion applications. Kurishita et. al. prepared ultrafine tungsten materials containing 0.25-0.8% TiC. The powders were fabricated by mechanical alloying (MA) and sintered by hot isostatic press (HIP). Improved mechanical properties as well as radiation resistance was demonstrated [18, 19]. Similar to conventional methods based on milling, MA also experiences problems with contamination and limitations in the powders uniformity in composition and morphology.

Alternatively, an extremely high degree of composition uniformity can be obtained by pre-mixing the elements in a precursor before the reduction using solution chemical methods. This bottom-up approach is in general carried out in two steps; a) Fabrication of uniform powder precursors containing ions of tungsten and the doping elements using solution processing methods such as spray-drying, freeze-drying or co-precipitation b) decomposition of the obtained precursors in reducing or carburizing atmospheres to W or WC based materials. The difference as compared to conventional processing can be illustrated with in an alternative flow sheet (Fig. 1.4).
Fig. 1.4, Bottom-up powder metallurgical processing of nanostructured tungsten based materials.

The hydrometallurgic route for the fabrication of tungsten containing intermediates, such as APT, can be modified to also include doping of other components such as Co, Ni, La or Y. The carburization is with advantage carried out in carbon-containing atmosphere during the decomposition of the precursor. The mechanical milling step conventionally used for fabrication of composite powders (Fig. 1.3), can be eliminated from the process flow sheet. These bottom-up methods offer several advantages such as control of the composition on the atomic scale resulting in very homogenous powder and the possibilities of modifying particle size and particle size distribution, during the solution processing step. The nanoscale can be obtained either in the solution chemical step or during the following processing step. There have been various reports on the solution processing methods for the fabrication of different tungsten based materials. Kear, McCandlish and co-workers at Rutgers University [22, 24, 25] developed a process for the fabrication of nanostructured WC-Co powders. The powder precursor is obtained via spray-drying of a homogenous aqueous solution containing a cobalt salt and highly soluble ammonium metatungstate. The processing of the precursor continues by reduction in hydrogen gas and carburization in a carbon containing atmosphere, e.g. a mixture of carbon monoxide and carbon dioxide, resulting in a nanostructured WC-Co powder. Another example is the process developed by Xi et. al. [26] for the fabrication of nanostructured tungsten powder containing rare earth oxides to be used for tungsten welding electrodes. The method starts from homogenous aqueous solutions of AMT and soluble rare earth salts such as lanthanum, cerium or yttrium nitrates. The solvent is removed by freeze drying. The resulting precursor powder is heated in hydrogen atmosphere to produce nanostructured tungsten powder alloyed with rare earth oxides. A major advantage of these evaporation based methods is that the ratio between the elements can be adjusted over a wide range, only limited by their solubility in the solution phase. A drawback is the relatively large particle size of the precursors, typically in the micron-range.

Zhu and Manthiram [27, 28] used another technique for the preparation of the precursor, where a gel of W and Co was mixed with polyacrylonitrile polymer, dried and heated to give an uniform mixture of nanoscale WC and Co. The method seems to be restricted to the preparation of small batches, possibly with only limited control of composition and homogeneity.

In methods based on co-precipitation techniques, the solution chemical conditions are tuned to result in the formation of a solid homogenous tungsten salt with a certain content of doping elements. The resulting powder precursor can be calcined to a mixed oxide and reduced under hydrogen gas to a uniform tungsten composite powder. Fait el. al. [29, 30] reported a method for the fabrication of potassium doped tungsten powder aimed at use for light filaments, starting by the crystallization of a mixed potassium ammonium paratungstate salt. Another process also
based on the synthesis doped ammonium paratungstate salts is the method reported by Iwase et.
al. [31] for the preparation of mixed cobalt tungsten powders starting from ammonium
paratungstate and cobalt nitrate. The key issue in these methods is to establish solution chemical
conditions able to produce materials with the desired characteristics. Similar to spray- and freeze-
drying techniques, powders can be made with controlled composition and homogeneity. In
addition, possibilities of further engineering of other aspects of the powders such as size on the
nanoscale, the crystal structure or controlled inhomogenities, are also available with co-
precipitation.

1.6 Precipitation of Tungsten Based Compounds from Aqueous Solutions

Hexavalent tungsten can in aqueous solutions, similar to hexavalent molybdenum and
pentavalent vanadium, undergo polymerization resulting in the formation of several different
polyanions. The oxoanion $\text{WO}_4^{2-}$ reacts with $\text{H}^+$, starting by the protonation to $\text{HWO}_4^-$, continuing with aggregation and condensation steps leading to the formation of various
oxometalates, e.g. isopoly anions containing $\text{W}$, $\text{H}$ and/or $\text{O}$, e.g. $[\text{W}_7\text{O}_{24}]^{12-}$ and
$[\text{H}_2\text{W}_{12}\text{O}_{42}]^{10-}$ around pH 5-7 and $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$ at pH values of 2-4. The overall formation reaction can be described as
in Eq. 1.6, where each species formed is defined by a specific $p/q$ value.

$$\text{p H}^+ + q \text{WO}_4^{2-} \rightleftharpoons [\text{H}_p\text{W}_q\text{O}_y]^n- + (4q-y) \text{H}_2\text{O} \quad (1.6)$$

A large number of different isopoly anions have been identified. The distribution between the
different species at equilibrium depends on several factors, such as acidity, total tungstate
concentration and temperature. These isopoly anions may also react further with other metal
ions, e.g. Co(II), Cu(II), Zn(II) or Mn(II), or oxoanions such as $\text{PO}_4^{3-}$, $\text{SiO}_3^{2-}$ or $\text{AsO}_3^{-}$, leading to
the formation of different heteropoly anions, like $[\text{CoW}_{12}\text{O}_{40}]^{6-}$, $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ or $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$ [32].
Negatively charged isopoly or hetero ions can also be obtained in solids by the addition of an
appropriate positive counter ion, as during the production of APT from tungsten ore (Eq. 1.1).

Further acidification of tungstate solutions below pH below 2 results in the formation of the
sparely soluble ($<10^{-3}$M) tungstic acid ($\text{H}_2\text{WO}_4$) which instantly precipitates as solid tungsten
trioxide hydrates (TTH) with different crystal structures and contents of water depending on the
conditions (Eq. 1.7).

$$\text{H}_2\text{WO}_4 \text{ (aq)} \rightarrow \text{WO}_3 \cdot n\text{H}_2\text{O (s)} \quad (1.7)$$

Industrially TTH, or solid tungstic acid, is prepared by the addition of hydrochloric acid to a
slurry of APT in water [1] (Eq. 1.8).

$$(\text{NH}_4)_10[\text{H}_2\text{W}_{12}\text{O}_{42}] \cdot 4\text{H}_2\text{O (s)} + 10 \text{HCl (aq)} + a \text{H}_2\text{O} \rightarrow$$

$$12 \text{WO}_3 \cdot n\text{H}_2\text{O (s)} + 10 \text{NH}_4\text{Cl (aq)} + (10+a-12n) \text{H}_2\text{O} \quad (1.8)$$

There also several reports on the preparation on the preparation nano-sized TTH either from
APT [33-36] or sodium tungstate (Na$_2$WO$_4$) [37].
1.6.1 Cobalt Tungsten Compounds

Several different types of cobalt tungstate compounds have been reported in the literature. The simple salt CoWO$_4$ (s) can be prepared by the addition of cobalt ions to a slightly alkaline solution of WO$_4^{2-}$. However, under these conditions there is also the possibility of formation of solid cobalt hydroxide (Co(OH)$_2$ (s)) [38], resulting in a mixed and inhomogeneous precipitate with an increased cobalt content. This may be avoided by the presence of a chelating ligand, like ethylenediamine (en). The compound Co(en)$_3$WO$_4$(s) has been prepared from CoCl$_2$, H$_2$WO$_4$ and ethylenediamine and used as precursor for nanostructured WC-Co powder [39].

The addition of Co$^{2+}$ ions to a hot, freshly acidified (pH $\sim$6) Na$_2$WO$_4$ solution leads to the formation of [H$_2$Co$_2$W$_{11}$O$_{40}$]$^{8-}$ anion. The preparation of this and three other cobalt centered Keggin anions was reported by Baker and McCutcheon in 1956 [40]. A continued acidification of the solution will result in the formation of [CoW$_{12}$O$_{40}$]$^{6-}$ with only one cobalt ion per anion. Two more complexes, [H$_2$Co$_2$W$_{11}$O$_{40}$]$^{7-}$ and [CoW$_{12}$O$_{40}$]$^{5-}$ can be obtained by oxidation of one cobalt ion inside each complex.

During the synthesis of the [H$_2$Co$_2$W$_{11}$O$_{40}$]$^{8-}$ anion, Baker et. al. [40] also observed the formation of a pink cobalt tungstate precipitate which appeared to be similar to the materials obtained by Rosenheim starting from cobalt sulfate and sodium paratungstate [41]. A corresponding pink precipitate obtained following the method of Baker, has been recrystallised and structure determined [42]. The structure was formed by paratungstate anion linked together by cobalt (II) ions, K$_6$[Co(H$_2$O)$_4$]$_2$[H$_2$W$_{12}$O$_{40}$]14H$_2$O. Several other different cobalt paratungstate complexes, containing Co$^{2+}$ and [H$_2$W$_{12}$O$_{40}$]$^{10-}$ ions, have in recent years been prepared and structurally determined. In most cases the crystals were obtained from aqueous solutions of Na$_2$WO$_4$, Co$^{2+}$ and H$^+$ [43-45]. The pH of the solutions appears to be slightly acidic or neutral, i.e. 5-7. The synthesis can also be made from (NH$_4$)$_6$[H$_2$W$_{12}$O$_{40}$], OH$^-$ and Co$^{2+}$ [46]. There are also several early reports on different cobalt tungstate salts prepared from paratungstate salts [41, 47], including a compound used as a precursor for the preparation of WC-Co alloys in a method reported by Iwase et. al [31]. The precursor was obtained by reacting soluble cobalt salts with ammonium paratungstate in an aqueous solution or suspension. The powder produced using the same technique was also investigated later by Kim et.al. [48]. The formation process was considered to proceed via a substitution reaction in which ammonium ions were partly replaced by cobalt ions. Iwase et. al reports that acid was produced during formation of the cobalt tungstate precursor and therefore recommended an initial addition of ammonium hydroxide to promote the formation of the final product by the neutralization of the released protons.

1.6.2 Rare Earth Tungsten Compounds

There are only a few reports on the preparation of rare earth tungstate solids from aqueous solution. One early example from 1904 is the work of Rogers and Smith who prepared a number of salts containing tungsten and other metal ions including ammonium lanthanum tungstate and ammonium cerium tungstate [49]. Later reports Razgon et. al. in 1980 [50] and Rozantsev et. al. in 1982 [51] described the preparation and characterization of several rare earth tungstates including lanthanum paratungstate.
1.6.3  Doped Tungsten Trioxide Hydrates

There are several early reports on the formation TTH solids precipitated together with other metal ions [52, 53]. More recently several alkali doped TTH have been prepared by hydrothermal methods and characterized structurally [54-58] as open frameworks built up by WO₆ octahedral building blocks. The unit cell may be cubic (pyrochlore) [55], hexagonal [54, 55] or orthorhombic [54] depending the synthesis conditions and the doping ions which can occupy channels within the structure.
1.7 **Scope of the Work**

The task has been to explore and develop new nanostructured tungsten composites by the use of solution chemical processing. The approach has been to fabricate powders in two steps:

a) The synthesis of uniform powder precursors containing ions of tungsten and the doping elements by co-precipitation from an aqueous phase

b) Further processing of the precursors into W or WC based nano-composite powders.

In general the objectives were to develop,

- Precursor powders with high degree of homogeneity, preferably with components mixed on the atomic scale.
- Materials with compositions which can be controlled and varied in a range relevant for the aimed application.
- Materials with a high degree of purity, achieved by elimination of the milling step and by the appropriate choice of starting materials.
- Powder precursors which can be processed into W or WC based powders with nano-scale.
- An economically favorable process easy to scale-up.

Two different types of materials have been chosen for this study;

I) Nanostructured WC-Co composites with a cobalt content from 3 to 10wt%. WC-Co materials have been made from two different types of precursors. Powder precursors based on the Keggin anion, $[\text{Co}_2\text{W}_{11}\text{O}_{40}]^8^-$, and cobalt salts of paratungstate, $[\text{H}_2\text{W}_{12}\text{O}_{42}]^{10^-}$, were reduced, carburized and sintered to solid WC-Co materials. Paratungstate based precursors were prepared with different cobalt contents corresponding to 3.7% - 10% Co in the final WC-Co composite. Further, grain growth inhibiting elements (V, Cr) were added directly to the precursor. The processing paratungstate-based powder precursors were also studied further in order to decrease the grain size of the obtained W-Co and WC-Co powders.

II) Nanostructured W-ODS composites aimed at use as plasma facing materials in future fusion energy power plant. W-ODS powders with $\text{La}_2\text{O}_3$ or $\text{Y}_2\text{O}_3$ have been made both from paratungstate- and TTH-based precursors. Precursors were characterised by SEM and thermal analysis in some detail. Nano-scale precursors were also processed and sintered to solid tungsten-based composites.
2 Methods

2.1 Synthesis of Precursors

Powder precursors were fabricated by co-precipitation from aqueous solution. The reactions were carried out in stirred solutions or suspension either at room temperature or at higher temperatures using heating mantles with temperature control. The solids were thereafter collected by filtration, in most cases washed with ethanol, and dried before further processing. The starting materials were commercial chemicals used without further purification.

2.1.1 Keggin-Based Cobalt Tungsten Precursors

The Keggin complex \([\text{H}_2\text{Co}_2\text{W}_{11}\text{O}_{40}]^8-\) was synthesized in aqueous solutions at 90-100°C with a pH around neutral from cobalt acetate and different tungsten salts; Route A starting from sodium tungstate (Na\(_2\)WO\(_4\)), Route B starting from ammonium tungstate solution ((NH\(_4\))\(_2\)WO\(_4\) (aq)) prepared by conversion of sodium tungstate solution (Na\(_2\)WO\(_4\) (aq)) using ion exchange and Route C starting from ammonium metatungstate (\((\text{NH}_4)\)\(_6\)[H\(_2\text{WI}_2\text{O}_{40}\) ]). The pH was adjusted by additions of acetic acid in Routes A and C, while ammonium hydroxide was used in Route C. The ammonium salt, \((\text{NH}_4)\)\(_8\)[H\(_2\text{Co}_2\text{W}_{11}\text{O}_{40}\) ] \(\cdot\) xH\(_2\)O, was obtained after the addition of ammonium acetate (NH\(_4\)Ac). Powders from Routes A and C where re-crystallized once before further processing to sintered WC-Co materials.

2.1.2 Paratungstate-Based Cobalt Tungsten precursors

W and Co containing paratungstate based precursors were synthesised from APT and cobalt hydroxide. The two solids, APT and Co(OH)\(_2\), were suspended in water with the initial weight ratio APT/water equal to 1/3. The suspension was stirred and at 90-100°C for 3 h, where after a homogenous cobalt-tungstate containing compound was filtered off. The solid washed with ethanol and dried at 80 - 100°C. W and Co containing precursors doped with V and Cr were synthesised from APT, cobalt hydroxide, vanadium (III) chloride and chromium perchlorate hexahydrate. APT and cobalt hydroxide were mixed with water and heated to 90°C as in described above. An aqueous solution of Cr(ClO\(_4\))\(_3\) was added after 1 h at 90°C. An ethanol solution of VCl\(_3\) was added after 1 hour more. The powder was filtered off after another 2.5 hrs at 90°C (totally 3.3 h), washed with ethanol and dried as above.

2.1.3 Paratungstate-Based Rare Earth Tungsten Precursors

W and La or Y containing paratungstate based precursors were prepared from APT and lanthanum or yttrium nitrate. APT as received, or after dehydration at 150°C, was suspended lanthanum or yttrium nitrate solutions with a initial weight ratio APT/solution ratio of 1/3. The reaction was carried out at room temperatures and at higher temperatures.

2.1.4 TTH-Based Rare Earth Tungsten Precursors

W and Y containing TTH bases precursors were prepared from APT, yttrium nitrate and nitric acid. APT was suspended in an yttrium nitrate solution at room temperatures. Concentrated nitric acid (65 %) was added under vigorous stirring and left to react for 30 min. The weight ratio APT/solution was 1/3. Ethanol was added and the suspension was stirred for another 3h.
2.2 Processing of Precursor

2.2.1 WC-Co Composites

Batches of powder precursors fabricated at KTH, were reduced, carburised and sintered at CermeP in Grenoble. Keggin-based precursors, were reduced at 750ºC in hydrogen, carburized in a mixed H₂/CH₄ atmosphere at 1000ºC, mixed with VC, compacted at 200 MPa and sintered at 1410ºC. Paratungstate-based precursors were reduced at 780ºC, carburized in hydrogen at 900ºC after mixing with carbon black, mixed with VC and Cr₃C₂, compacted at 200 MPa and sintered by HIP at 1450ºC and 6 MPa. The reduction of paratungstate-based precursors was also investigated at 600, 650 and 700ºC in hydrogen atmosphere (400 ml/min). Powders reduced at 700ºC for 3h were also carburized mixed carbon monoxide/carbon dioxide atmospheres (400 ml/min), varying the CO/CO₂ ratio.

2.2.2 W-Y₂O₃ Composites

W and Y containing TTH-based precursor were calcined in nitrogen at 450ºC, reduced at 600ºC and 800ºC in hydrogen atmosphere (400 ml/min). The reduced powder were sintered under vacuum using spark plasma sintering (SPS), Dr. Sinter 2050 (Sumitomo Coal Mining Company). A graphite die of 12 mm inner diameter was used. The sample was kept at 600ºC for 3 min. The temperature was ramped at the rate of 50ºC/min to 1100ºC and held for 3 min under a pressure of 50 MPa.

2.3 Materials Analysis and Characterization

2.3.1 Composition and Structure

The W and Co composition of starting materials APT and Co(OH)₂ for WC-Co materials, were determined gravimetrically after calcination at 800ºC. Fabricated powders were characterized by chemical and structural analysis. The elemental composition (W, Co, V, Cr, Y, La) were determined by inductive coupled plasma (ICP-OES) after dissolving the samples in aqueous solutions. X-ray diffraction (XRD) was carried out to identify or determine the phase content of the obtained powders.

2.3.2 Particle Size and Morphology

Size and morphology were mainly determined by scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDX) and transmission electron microscopy (TEM). Crystallite size of WC grains was estimated from XRD data by the use of Scherrer’s equation. The particle size was also calculated from specific surface areas assuming spherical particles. The surface area was determined by nitrogen adsorption using the BET-model for data interpretation.

2.3.3 Thermal stability and reactivity

The decomposition of precursors was studied by thermal gravimetric analysis (TGA), as a function of temperature and time in different atmospheres (50-100 ml/min of air, N₂ or 5%H₂) to determine thermal stability and reactivity. Gases released from solids during decomposition in TGA were identified by evolved gas analysis (EGA), connecting the TGA furnace to a FTIR instrument via a heated gas transfer line. The gas passed with a flow of 50 ml/min though a gas cell within the spectrometer which continually collected spectrums with intervals of 11 s.
3 Results and Discussion

3.1 Fabrication of WC-Co Materials via Chemical Processing (Papers I+II)

3.1.1 Keggin-Based Precursors

3.1.1.1 Synthesis

A method for the fabrication of precursors containing \([H_2Co_2W_{11}O_{40}]^8\), was developed and patented [59]. The green colored Keggin-complex was prepared in several different synthetic routes starting from different tungstate solution. Powders of \((NH_4)_8[H_2Co_2W_{11}O_{40}]\ _{xH_2O} (s)\) was obtained by the addition of ammonium acetate. The route (Route A) starting with sodium tungstate \(Na_2WO_4\), as in the method of Baker and McCutcheon [40], resulted in high yields but also rather high contents (0.2-0.4 %) of sodium in the precursor even after a recrystallization step. Other preparation routes starting with sodium free solutions were also tested. One alternative (Route B) was the use of ion exchange techniques converting the starting sodium tungstate solution to an ammonium tungstate \((NH_4)_2WO_4\)-solution. A third alternative (Route C) started from ammonium metatungstate (AMT). Route B and C resulted in sodium free powders of the green target compound \((NH_4)_8[H_2Co_2W_{11}O_{40}]\ _{xH_2O} (s)\) but also precipitation of a second grey/pink solids containing both cobalt and tungsten. The results of the synthesis using the different routes are summarized in Table 3.1.

Table 3.1, Synthesis of \((NH_4)_8[H_2Co_2W_{11}O_{40}]\ _{xH_2O}\)

<table>
<thead>
<tr>
<th>Route</th>
<th>Starting Materials</th>
<th>Composition of Oxometalate Salt</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>W (%)</td>
</tr>
<tr>
<td>A</td>
<td>(Na_2WO_4)</td>
<td>66</td>
</tr>
<tr>
<td>B</td>
<td>((NH_4)2WO_4)</td>
<td>64</td>
</tr>
<tr>
<td>C</td>
<td>((NH_4)<em>6[H_2W</em>{12}O_{40}])</td>
<td>66</td>
</tr>
</tbody>
</table>

\(^1\)Very low concentration, no accurate analysis

The formation of \([H_2Co_2W_{11}O_{40}]^8\) sodium tungstate, cobalt acetate and acetic acid can be described as in Eq. 1.

\[
2Co^{2+} + 11WO_4^{2-} + 10H^+ \Rightarrow [H_2Co_2W_{11}O_{40}]^8 + 4H_2O \tag{3.1}
\]

The mechanism of the reaction is not known, however dominating isopoly species under these conditions is heptatungstate which forms quickly when \(H^+\) is added to \(WO_4^{2-}\) as in Eq. 2 [32].

\[
7WO_4^{2-} + 8H^+ \Rightarrow [W_7O_{24}]^{6-} + 4H_2O \tag{3.2}
\]
The cobalt ion can presumably react with \( W_7O_{24}^{6-} \) and/or with fragments of the heptamer such as the hexamer \([H_3W_6O_{22}]^{5-}\) and the pentamer \([HW_5O_{19}]^{7-}\) to give the green coloured dicobalt tungstate complex.

Route B started with \((NH_4)_2WO_4\) (aq) prepared via ion exchange of a Na\(_2WO_4\) solution. In this case, the addition of cobalt acetate and acetic acid resulted in the formation of the soluble \([H_2Co_2W_{11}O_{40}]^{6-}\) complex but also in precipitation of grey and pink solids containing both cobalt and tungsten. Route C started with a solution of \((NH_4)_6[H_2W_{12}O_{40}]\). The pH was in this case adjusted to neutral by an addition of ammonium hydroxide. The reaction gave the green solution of the \([H_2Co_2W_{11}O_{40}]^{6-}\) complex (Eq. 3) and similar to Route C, also a pink solid.

\[
\frac{11}{12} [H_2W_{12}O_{40}]^{6-} + 2 Co^{2+} + \frac{78}{12} OH^- \rightarrow [H_2Co_2W_{11}O_{40}]^{6-} + \frac{122}{12} H_2O \quad (3.3)
\]

The pink color indicates that the solid obtained as a side product in Routes B and C, containing cobalt in positions with octahedral coordination. The green species \([H_2Co_2W_{11}O_{40}]^{6-}\) also has one cobalt occupying the tetrahedral position in the center of the complex. Baker et. al. also observed a second solid in the synthesis starting from sodium tungstate (Route A) \[40\]. The corresponding compound has later been recrystallized and indentified as a cobalt paratungstate salt \[42\]. The dodecaparatungstate anion \([H_2W_{12}O_{42}]^{10-}\) can be formed from heptatungstate (Eq. 7).

\[
12 [W_7O_{24}]^{6-} + 2 H^+ + 6 H_2O \rightleftharpoons 7 [H_2W_{12}O_{42}]^{10-} \quad (3.4)
\]

The distribution between hepta- and dodeca- paratungstates are at higher temperatures strongly shifted to the heptamer. The concentration of the dodecamer is, in aqueous solutions equilibrated close to the boiling point, actually below the detection limits of the NMR methods used for investigation of isopolytungstates in solution \[60, 61\]. However, the solubility of dodecaparatungstate salts is in general much lower than of corresponding salts of heptaparatungstate, mononutungstate or metatungstate. Precipitation e.g. ammonium or sodium paratungstate may therefore occur even when the concentration of the dodecaparatungstate anion is rather low. Alternatively, cobalt ions may also coordinate to the dodecaparatungstate anion and precipitated as insoluble cobalt paratungstate salts (Eq. 4) competing with the formation of \([H_2Co_2W_{11}O_{40}]^{6-}\).

\[
x Co^{2+} + (10-2x) M^+ + [H_2W_{12}O_{42}]^{10-} \Rightarrow Co_xM_{(10-2x)}[H_2W_{12}O_{42}] \quad (3.5)
\]

\( M^+ = NH_4^+/Na^+ \)

### 3.1.1.2 Reduction, Carburization and Sintering

Precursors from Routes A and C were reduced, carburized and sintered into a solid WC-Co material. The precursor morphologies can be described as mixture of porous and dense particles with a size of 5-10 \(\mu m\) in agglomerates of 20-50 \(\mu m\) (Figs. 3.1 and 3.2). Reduction at 750°C in hydrogen atmosphere resulted in pseudomorphs of the original precursors, composed of submicron grains (SEM micrographs). Carburization at 1000 °C in H\(_2\)/CH\(_4\) atmosphere and sintering at 1410 °C resulted in both cases a uniform submicron microstructure of WC-Co. A
small amount (0.4 %) of C powder was added as a grain growth inhibitor before the sintering step (SEM micrographs). A slightly larger grain sizes were observed in Route A, as compared to Route C, after reduction, carburization as well as after the sintering step. The increased grain size is most likely an effect of presence of sodium, a well-known grain growth enhancer [1]. The composition of the carburized powders and properties of the sintered materials are summarized in Table 3.2.

Fig. 3.1, SEM Micrographs showing morphologies during the different steps of Route A; a) powder precursor, b) reduced powder , c) carburized powder and d) sintered material
Fig. 3.2 SEM Micrographs showing morphologies during the different steps of Route C; a) powder precursor, b) reduced powder, c) carburized powder and d) sintered material

<table>
<thead>
<tr>
<th>Table 3.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Properties after different processing steps</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition after carburisation</th>
<th>Properties of the sintered materials</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Co (%)</td>
<td>Na (ppm)</td>
</tr>
<tr>
<td>A</td>
<td>5.43</td>
<td>20</td>
</tr>
<tr>
<td>C</td>
<td>5.20</td>
<td>&lt;3</td>
</tr>
</tbody>
</table>
3.1.2 Paratungstate-Based Precursors

3.1.2.1 Synthesis

The fabrication of tungsten carbide-based composites via paratungstate-based precursors was suggested in the patent by Iwase et al. from 1969 [31], which describes the synthesis of precursors from suspensions of ammonium paratungstate, soluble salt of e.g. cobalt and for pH adjustment ammonium hydroxide. Several patents on similar but improved techniques have also been filed by KTH [59, 62, 63].

The present study describes a further development using solid cobalt hydroxide as the source of cobalt ions [64]. Homogenous powder precursors containing W and Co has been synthesized by suspending the starting solids in water at 90-100°C. A new solid with flake shaped particles with 5-20 μm sides and less than 1 μm thickness (Fig. 3.3), containing the two metal ions, was formed and filtered off after 3h. The reaction solution contained small amounts of tungsten (50-200mM) and negligible amounts of cobalt (< 1 mM) after reaction completion (Fig. 3.4).

Fig. 3.3, SEM Micrograph of paratungstate-based W and Co containing precursor

![Fig. 3.3, SEM Micrograph of paratungstate-based W and Co containing precursor](image)

![Fig. 3.4, Synthesis of W-Co salts from APT and cobalt hydroxide](image)

Fig. 3.4, Synthesis of W-Co salts from APT and cobalt hydroxide

The W to Co ratio in the obtained powders could be varied and controlled by varying the initial ratio between APT and cobalt hydroxide. Also the amount of tungsten dissolved in the aqueous phase was found to be a function of the APT to cobalt hydroxide ratio, an increase of the amount of cobalt hydroxide resulted in lower concentrations of tungsten in solution. Fig. 3.5 shows the concentration of tungsten in solution after 3 hrs reaction as a function of the atomic ratio, W/Co, in the obtained powder precursor determined by ICP. Synthesis of materials of new
compositions was greatly helped by the almost linear relation between the W/Co ratio in the product and the concentration of W in solution after reaction completion. The amount of dissolved tungsten was relatively small (3-15% of the total amount) and did not need to be known or controlled with great accuracy. Powders with several different W and Co ratios were prepared, ranging from 2.7 to 7.8 corresponding to Co contents in WC-Co from 10 to 3.7%.

Fig. 3.5, Concentration of W in solution as a function the atomic ratio, W/Co, in the final powder

The process can be described as a solvent mediated transformation in which solid APT and cobalt hydroxide in suspension is converted into solid containing ions of both W and Co. The final pH of the synthesis suspension varies from 7 to 9, increasing with the amount of cobalt hydroxide. The transformation starts by dissolution of cobalt hydroxide (Eq. 3.6) and ammonium paratungstate (Eq. 3.7).

\[
\text{Co(OH)}_2 (s) \rightarrow \text{Co}^{2+} + 2 \text{OH}^{-} \quad (3.6)
\]

\[
(\text{NH}_4)_{10}[\text{H}_2\text{W}_{12}\text{O}_{42}] \cdot 4\text{H}_2\text{O} (s) \rightarrow 10 \text{NH}_4^+ + [\text{H}_2\text{W}_{12}\text{O}_{42}]^{10-} + 4\text{H}_2\text{O} \quad (3.7)
\]

The paratungstates ion precipitates with ammonium and cobalt as counter ions as a solid contain both W and Co. Thermodynamic modelling indicate the formation cobalt-amine in the synthesis solution. Consequently, the solid may contain ammonium ions as well as ammonia molecules as indicated in Eq. 3.8. Binding of ammonia to the solid would also result in the release of H\(^+\) to the solution as also reported by Iwase et.al. [31].

\[
(10-2a+y) \text{NH}_4^+ + a \text{Co}^{2+} + [\text{H}_2\text{W}_{12}\text{O}_{42}]^{10-} \rightarrow (10-2a+y) \text{NH}_4\text{Co}_a\text{NH}_{3+y}[\text{H}_2\text{W}_{12}\text{O}_{42}] \cdot z\text{H}_2\text{O} (s) + y \text{H}^+ \quad (3.8)
\]
The colour of the precipitate is pink, a clear indication showing that of the cobalt ions are located in octahedral positions within the solid. However, solids with a low cobalt content (W/Co = 7.8), changed from pink to brown/green during the process, a sign of oxidation of Co(II) to Co(III).

W and Co containing precursors doped by small amounts of Cr and/or V, were prepared using a modified preparation route. The synthesis started with the reaction between APT and cobalt hydroxide as when preparing pure W-Co precursors. Solutions of chromium (III) perchlorate and/or vanadium (III) chloride was added to during the process. Tungsten and vanadium were found both in the powder and the liquid phase after completing the synthesis. Cobalt and chromium were completely precipitated.

3.1.2.2 Processing and Evaluation of Sintered Materials

The precursors were reduced under hydrogen at 780°C and carburised under hydrogen after mixing with solid carbon at 900°C. The flake particles (5-20 µm, Fig. 3.3) were broken during the reduction giving small spherical particles (200 nm, Fig. 3.6) in agglomerates of about the same shape and size as the original particles. The flake agglomerates dispersed by a milling step resulting in 1 µm - sized agglomerates of 0.2 µm particles (Fig. 3.7). Carburisation (Fig., 3.8) and sintering (Fig., 3.9), resulted in highly uniform microstructures with fine tungsten carbide grains size < 1 µm.

![Fig. 3.6, SEM Micrograph of reduced powder](image)

![Fig. 3.7, SEM Micrograph of reduced and lab milled powder](image)
Small amounts of VC (0.6%) and Cr₃C₂ (0.3%) were added to the WC-Co powders to limit the grain growth during sintering. Tab. 3.3 shows the some properties of sintered material with 6.2% cobalt. The mechanical properties are comparable with those of conventional submicron (0.5-0.9 μm) WC-Co grades.

Table 3.3
Properties of sintered material prepared from paratungstate-based precursor

<table>
<thead>
<tr>
<th>Composition after carburization</th>
<th>Properties of the sintered material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co (%)</td>
<td>C tot (%)</td>
</tr>
<tr>
<td>6.24</td>
<td>5.68</td>
</tr>
</tbody>
</table>

3.1.2.3 Processing of the Precursor into WC-Co Nanopowder

The processing of paratungstate-based powder precursors was also studied further in order to decrease the grain size of the obtained W-Co and WC-Co powders. Precursors were prepared with the atomic ratio W/Co equal to 4.8, corresponding 5.9% Co in the final WC-Co, reduced at 600, 650 and 700°C in H₂ and carburized at 700°C in a mixtures of CO and CO₂ gas. Complete reduction of the precursor to W-Co was carried out within less than 3 h at 650 and 700°C, while longer time was needed at 600°C (Fig. 3.10). The specific surface area (BET-method) of the reduced powders was increasing with decreasing reduction temperature (8.7 m²/g at 700°C, 15 m²/g at 650°C and 18 m²/g at 600°C). The particle size of the reduced powders, based on the surface area, was 38 nm at 700°C, 22 nm at 650°C and 18 nm at 600°C.
Fig. 3.10, X-ray diffraction pattern of paratungstate based precursor (W/Co = 4.8) reduced in H₂ at different temperatures.

Powders reduced at 700°C in H₂, were also carburized at 700°C during 3h in CO/CO₂ – mixtures with 70, 80 or 90% CO gas. The carburization rate increased with increasing CO content or i.e. with increasing carbon activity (Fig. 3.11). The reaction path can be described as:

\[
\text{W-Co} \rightarrow \text{W}_6\text{Co}_6\text{C} \rightarrow \text{W}_3\text{Co}_3\text{C} \rightarrow \text{W}_2\text{C-Co} \rightarrow \text{WC} - \text{Co}
\]

Complete carburization was observed with 90% CO. However, these high levels of carbon activity also results in the precipitation of free carbon. A further optimization of the CO/CO₂ and temperature would be required for the fabrication stoichiometric WC.

Fig. 3.11, X-ray diffraction pattern of powders reduced at 700°C in H₂ and thereafter carburized at 700°C in and different CO/CO₂ mixtures.

The grain size and the morphology of the carburized sample was investigated by several different methods. The measured BET-surface (8.1 m²/g), corresponded to spherical particles with a size of 50 nm, while calculations based on the broadening of the XRD peaks indicated a crystallite size of 20-30 nm. TEM micrographs confirmed this finding Fig (3.12).
3.2 Fabrication of ODS-Tungsten Composite Powder via Chemical Processing (Papers III+IV)

3.2.1 Paratungstate-Based Precursors

3.2.1.1 Synthesis

Rare earth doped paratungstate-based precursors were prepared using two different methods. In the first APT, as received, was suspended in lanthanum nitrate solutions. Treatment of APT in 14 mM La(NO₃)₃ for 24 h resulted in a solid of containing 69 wt% W and 0.5 % La, corresponding to atomic ratio W/La of 104. SEM micrographs and diffraction patterns show that morphology and crystal structure did not change significantly from starting material. The reaction was also carried out at 50°C for 5h, and the resulting powders were similar to that prepared at room temperature.

In the second method, the APT·4H₂O was first heated at 150°C to remove crystalline water resulting in a weight loss of 1.8 - 2 %, before suspension in the rare earth nitrate solution. Suspension of dehydrated APT in lanthanum nitrate as well as yttrium nitrate solutions, resulted in a change of the morphology, but also in the absorption of lanthanum or yttrium ions into the powder both at room temperature and at 80°C. The APT-particles were found to crack and fracture during the treatment in solution. In addition, a new type of plate-like particles was also observed after reaction at 80°C. The concentration of the cation in the precursors could be controlled by the varying its concentration in the reaction solution. Table 3.4 displays the different samples prepared with varying Y-concentration, using dried APT and reaction at 80°C for 3 hours. Fig. 3.13 shows the diffraction patterns and Fig. 3.14 SEM micrographs of the three powder precursors from Table 3.4.
Table 3.4

<table>
<thead>
<tr>
<th>Powder precursors</th>
<th>Conc. of [Y] in solution (mM)</th>
<th>Y (wt %)</th>
<th>W (wt %)</th>
<th>W/Y (atomic ratio)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>27</td>
<td>0.56</td>
<td>71.9</td>
<td>62</td>
</tr>
<tr>
<td>II</td>
<td>53</td>
<td>1.4</td>
<td>71.5</td>
<td>25</td>
</tr>
<tr>
<td>III</td>
<td>148</td>
<td>3.05</td>
<td>70.7</td>
<td>11</td>
</tr>
</tbody>
</table>

Fig. 3.13, X-Ray Powder diffraction pattern of precursors with different yttrium contents: Precursor I, Precursor II and Precursor III (Tab. 3.4). Arrows marking new phase formed.
Fig. 3.14, SEM micrographs of powder precursors with different yttrium content, a) Precursor I, b) Precursor II and c) Precursor III (Tab. 3.4)
Diffraction patterns (Fig. 3.14) reveal that, as in the first method, the main phase in Precursors I-III had the same monoclinic structure as the starting material APT. Furthermore, additional peaks indicating the formation of a new phase, was observed in Precursors I but most clearly seen in Precursor II. The parameters for an orthorhombic unit cell which could be determined to \( a = 19.3 \, \text{Å}, \, b = 15.4 \, \text{Å} \) and \( c = 10.3 \, \text{Å} \), using six reflections from Precursor II. The pattern of Precursor III also shows one broad additional peak at \( 2\theta = 6.9^\circ \) \( (d = 12.7 \, \text{Å}) \), slightly shifted as compared to the corresponding peak in patterns of Precursors I and II. The observation of a second phase is also consistent with SEM images of Precursor I and II showing fractured APT-like particles but also a second plate-shaped phase, found to contain yttrium [65]. The particles in Precursor III appear to be less fractured and covered with very small particles with a size of 200-300 nm.

In the first synthesis method, where ammonium paratungstate tetrahydrate (APT·4H₂O) was used, the preservation of the original unit cell and morphology suggests that the doping process takes place via adsorption of La³⁺ ions onto the surface of the APT·4H₂O grains. In the second synthesis route, starting from dehydrated APT, changes in SEM and XRD data indicate a different reaction path for Precursors I and II involving transformations of both morphology and crystal structure. The cracking and fracturing of APT particles may be an effect of rapid rehydration as the dehydrated particles are suspended in water. The formation of new plate-shaped yttrium containing particles, also suggests partial dissolution of APT particles into \( \text{NH}_4^+ \) and \( [\text{H}_2\text{W}_{12}\text{O}_{42}]^{10-} \) which can react with \( \text{Y}^{3+} \) and precipitate as a new phase. The dehydration of the APT may increase the APT dissolution rate, thus facilitating transformation via the aqueous phase. In the case of Precursors III, where the yttrium concentration in solution is higher, the reaction with \( \text{Y}^{3+} \) appears to be mostly located to the surface of the APT particles as in the first synthesis method starting from hydrated APT.

### 3.2.1.2 Thermal Decomposition in Air

Fig. 3.15 is showing the TG and DTG curves of Precursors I, II and III and pure APT decomposing in air. The samples were heated from room temperature to 600°C at a rate of 5°C/min. The different materials lost weight through release of water and ammonia gas in several steps from start up to about 500°C. The final result is a mixture of yttrium and tungsten oxide. The overall decomposition process can be given by Eq. 3.9.

\[
\text{(NH}_4\text{)}_{10-3a}\text{Y}_a[\text{H}_2\text{W}_{12}\text{O}_{42}] \cdot b \text{ H}_2\text{O} \Rightarrow \\
\frac{a}{2} \text{Y}_2\text{O}_3 (\text{s}) + 12 \text{WO}_3 (\text{s}) + (10-3a) \text{NH}_3 (\text{g}) + (6-\frac{3a}{2}+b) \text{H}_2\text{O} (\text{g})
\] (3.9)

The number of ammonium ions per formula unit was calculated by charge balance, knowing the yttrium and tungsten contents as determined by chemical analysis (Tab. 3.4). The water content was for each compound determined from total weight loss at 500°C. It was found that the number of water molecules \( (b) \) increases linearly with the amount of yttrium \( (a) \) in each formula unit as \( b = 6.8a + 2.6 \). Hence, there is one type of water which varies with the amount of yttrium and another which is independent of the yttrium content. The general molecular formula can be written as \( \text{(NH}_4\text{)}_{10-3a} \text{Y(H}_2\text{O})_{6.8a} \text{[H}_2\text{W}_{12}\text{O}_{42}] \cdot 2.6 \text{H}_2\text{O} \), with the coefficient \( a = 0.19, 0.48 \) and \( 1.07 \) for precursors I, II and III, respectively. In average there are 6.8 water molecules associated with...
each yttrium ion. The additional 2.6 water molecules should occupy positions corresponding to the locations of water in pure APT.

![Graph showing TG and DTG curves of APT, Precursors I, II, and III obtained in air atmosphere at a heating rate of 5°C/min.](image)

Fig. 3.15, TG and DTG curves of APT, Precursors I, II, and III obtained in air atmosphere at a heating rate of 5°C/min.

3.2.1.3 Thermal Decomposition in 5% H₂

Figures 3.16 and 3.17 shows the TG curves of Precursors I and III decomposing in inert followed by reducing atmosphere. As seen, the rate of reduction was found to vary considerably, also between different samples taken from the same batch. Precursor I tend to the display a shorter reduction time than Precursor III for most, but not all, samples. This behavior is probably due to differences in particle size. Precursor I contains both small (< 1 µm) and large (20-50 µm) particles, while Precursor III mainly consist of particles of larger size (30-100 µm) (Fig. 3.14). In general, a decreasing decomposition rate could be observed below 83 wt% corresponding to an average stoichiometry of WO₂, most clearly seen for the slow reducing samples. The reduction of tungsten oxide in hydrogen atmosphere is known to progress stepwise from WO₃ to W, e.g. as given by Eq. 3.10 and 3.11. The last step from WO₂ to W is slow and often rate determining for the whole process (Eq. 3.11).

\[
\text{WO}_3 (s) + \text{H}_2 (g) \rightleftharpoons \text{WO}_2 (s) + \text{H}_2\text{O} (g) \tag{3.10}
\]

\[
\text{WO}_2 (s) + 2 \text{H}_2 (g) \rightleftharpoons \text{W} (s) + 2 \text{H}_2\text{O} (g) \tag{3.11}
\]
The nucleation of the W phase is critically dependent on the composition of the atmosphere, i.e., the ratio of water and hydrogen partial pressures ($P_{\text{H}_2\text{O}}/P_{\text{H}_2}$). For the reaction to proceed, water molecules formed in the reaction must be efficiently transported away from the reaction zone. A larger particle size results in an increased resistance to water transport. No consistent trend could be observed for the reduction rate dependence on the sample size.

Fig. 3.16, TG and temperature curves showing the decomposition and reduction of Precursor I

Fig. 3.17, TG and temperature curves showing the decomposition and reduction of Precursor III
3.2.2 Tungsten Oxide Hydrate-Based Precursors

3.2.2.1 Synthesis

A different type of precursor based on tungsten trioxide hydrates (TTH), were prepared under strongly acidic conditions. The synthesis started by suspending APT powder in an aqueous solution of yttrium nitrate at room temperature. Addition of nitric acid results in an instant formation of a white gel which thereafter changes into a light yellow suspension. The process can be understood as going through the following steps; i) dissolution of APT under release of paratungste ions to the aqueous phase (Eq. 3.12), ii) transformation of paratungstate ions to tungstic acid (Eq. 3.13) and iii) precipitation of tungstic acid as solid tungsten trioxide hydrate (Eq. 3.14).

$$\text{(NH}_4\text{)}_{10}\text{[H}_2\text{W}_{12}\text{O}_{42}\text{]} \cdot 4\text{H}_2\text{O} \text{ (s)} \rightarrow$$

$$10\text{NH}_4^+ + [\text{H}_2\text{W}_{12}\text{O}_{42}]^{10-} + 4\text{H}_2\text{O} \quad (3.12)$$

$$[\text{H}_2\text{W}_{12}\text{O}_{42}]^{10-} + 10\text{H}^+ + 6\text{H}_2\text{O} \rightarrow 12\text{H}_2\text{WO}_4 \text{ (aq)} \quad (3.13)$$

$$\text{H}_2\text{WO}_4 \text{ (aq)} \rightarrow \text{WO}_3 \cdot n\text{H}_2\text{O} \text{ (s)} \quad (3.14)$$

When the reaction is carried out in the presence of $\text{Y(NO}_3\text{)}_3 \text{ (aq)}$, $\text{Y}^{3+}$ ions are randomly incorporated within or adsorbed on the surface of the TTH nanoparticles, resulting, in either case, in the formation of a very uniform mixture of yttrium and tungsten ions. Tungstic acid is only sparsely soluble ($K_s<10^{-3} \text{ M}$) and precipitates at a high nucleation rate resulting in the formation of particles with a size of 25 nm or less, as shown by TEM (Fig. 3.18). As a last step during the synthesis, ethanol was added to the suspension to stop further growth of the particles. The primary particles were found to form agglomerate of 200-500 nm, as observed in SEM (Fig. 3.21a). Chemical analysis by ICP showed that the powder contained W and Y at an atomic ratio of W/Y=46.4, corresponding to a content 1.2 % Y$_2$O$_3$ in the final W-Y$_2$O$_3$ material.
Fig. 3.18, TEM images of precursor showing an overview of nanosized polycrystalline material (a), figure (b) shows nanosized crystalline material surrounded by some amorphous material.

3.2.2.2 Thermal Decomposition in Nitrogen

Fig. 3.19 shows the TG and DTG curves for the decomposition of tungsten trioxide hydrate based precursors in nitrogen atmosphere. Evolved gas analysis (EGA) by FTIR revealed release of H$_2$O in the first step, followed by N$_2$O and H$_2$O between 167 °C and 277 °C and H$_2$O in the final step up to 490°C (Fig. 3.20). In addition, traces of HNO$_3$ and NH$_3$ were also detected. Loss of water is observed at temperatures below 167 °C corresponding to 1.0 mole of H$_2$O per mole of WO$_3$. The formation of N$_2$O occurs at temperatures between 167 and 277 °C, as a result the decomposition of ammonium nitrate, a reaction known to generate N$_2$O and H$_2$O above 200°C [66]. The synthesis suspension contains 1 mole/L of NH$_4$NO$_3$ after the addition of the nitric acid of which a certain fraction can end up in the solid during its formation. The loss of 5.2 wt% corresponds to 0.18 mole NH$_4$NO$_3$ per mole of WO$_3$. Ammonium nitrate is known to be unstable and explosive under certain conditions [67]. For the up-scaling of the process hydrochloric acid should be considered instead of nitric acid, to avoid the formation of ammonium nitrate. The final weight loss step between 277 and 490°C is consistent with the crystallization of anhydrous tungsten oxide under the release of small amounts of water but also traces of ammonia around 300 °C and nitrous oxide at 415 °C.
Fig. 3.19, TG and DTG curves showing thermal decomposition of the precursor in N₂ atmosphere.

Fig. 3.20, FTIR absorbance of H₂O, N₂O, HNO₃ and NH₃ evolved during the thermal decomposition of the precursor in nitrogen atmosphere.
3.2.2.3 Reduction, Sintering and Characterization

Thermal processing of the precursor in nitrogen atmosphere follow by hydrogen atmosphere resulted in the formation of powder consisting of particles with two different morphologies, (i) larger particles, 200-300nm, with a cube morphology, and (ii) finer particles (< 50 nm) with both spherical and cubic shape, as shown in Fig. 3.21b. The In-lens backscattered electron signals (Z contrast) in the SEM revealed that fine spherical and cubic shaped particles have similar composition. X-ray diffraction confirmed that the main phase formed was tungsten metal [1]. However, an additional weak peak appeared at \( 2\theta = 43.91^\circ \) (\( d = 2.06 \ \text{Å} \)), indicating traces of \( \beta \)-tungsten in the powder. The position corresponds to the phase’s second most intense reflection, (112), while its most intense reflection, (012), is overlapping with

![SEM micrographs](image)

Fig 3.21, SEM micrographs for the (a) the formed powder precursor, (b) reduced powder showing bimodal morphology
Fig. 3.22, Diffraction pattern of reduced powder tungsten’s (110). β-tungsten is metastable and known to be stabilized by the presence of other elements [1], in this case likely to be yttrium. No reflections were detected for Y$_2$O$_3$ (Fig. 3.22).

The formation of cubic shaped particles suggests a growth mechanism by chemical vapor transport (CVT) via the gaseous WO$_2$(OH)$_2$ formed though reaction between different tungsten oxides and water vapor produced in the reduction process. The finer reduced particles have a shape similar to the precursor particles’, indicating a different formation mechanism in which oxygen is removed directly from the solid.

The reduced powders were consolidated by SPS at 1100°C to form a W-Y$_2$O$_3$ composite with a density of 16.3 corresponding to a relative density of 88%. Polished sample surface shows uniform distribution of oxide particles in bulk sample (Fig. 3.23a). EDX analysis reveals that the oxides are mainly accumulated at micro-porosities at tungsten grain boundaries. The highly uniform distribution of oxides in the sintered bulk material is an indication of uniform mixing of W and Y during the synthesis of the precursor. Channeling contrast (Fig. 3.23b) analysis of polished sample surface showed that nanosized subgrains and oxide nanoparticles are distributed within the tungsten grains (pointed by arrows). It is obvious from high resolution electron microscope images (Fig. 3.23b) that the oxide nanoparticles are also distributed within the tungsten grains. The inclusion of oxide particles most likely takes place during the formation of the previously described cube-shaped tungsten particles.
Fig 3.23, (a) Low magnification BSE image showing porosity and oxide distribution in sintered sample, (b) high resolution image showing subgrain features and oxide nanoparticles within tungsten grains pointed by arrows
4 Conclusions

Nanostructured tungsten composites have been fabricated via solution chemical processing. Several different routes based on co-precipitation, were developed and tested. Two different materials have been considered.

I) Highly homogenous W and Co containing powder precursors for WC-Co composites were prepared via two different routes. Keggin-based precursors were made from sodium tungstate or ammonium metatungstate and cobalt acetate. The composition of the precursors corresponded to 5.2 % Co in the final WC-Co composites. The precursor consisted of particles with a size of 5-10 μm in agglomerates with sizes up to 50 μm. Paratungstate-based precursors were prepared from ammonium paratungstate (APT) and cobalt hydroxide with different compositions corresponding to 3.7 to 9.7 % Co in the WC-Co material. Optional, small amounts of grain growth inhibiting elements such as Cr and/or V could also be added during the synthesis. The precursor particles had a plate-like morphology with 5-20 μm edges and less than 1 μm thickness. Both types of precursors were reduced in hydrogen at 750-780°C. Powders obtained using Keggin-based powders were carburized in CH₄/H₂ at 1000°C, while powders from paratungstate-based precursors were carburized in hydrogen at 900°C after mixing with carbon black. Sintering at 1410-1450°C resulted in WC-Co materials highly uniform microstructures with tungsten grain size less than scale 1 μm and hardness (1848-1957) and fracture toughness (8.6-9.1) values similar to those of conventional submicron (0.5-0.9 μm) WC-Co grades. The processing of paratungstate-based precursors was also further investigated. Nanostructured WC-Co powders with grains size of less than 50 nm by decreasing processing temperatures and by applying gas phase carburization.

II) W-ODS materials were fabricated starting from APT and lanthanum or yttrium nitrates. Paratungstate-based precursors were prepared with different homogeneity and particle sizes. The degree of the chemical uniformity varied with the particle size from ca 1 to 30 μm. Tungsten trioxide hydrate-based precursors, made from APT and yttrium nitrate under acidic conditions, had dramatically higher homogeneity and smaller particle size. The crystallite size was decreased to a few nanometers. These precursors were further processed to composite nanopowder and sintered to uniform W-1.2%Y₂O₃ composite material with a relative density of 88%. The microstructure has tungsten grain of less than 300 nm and nanosized oxide particles uniformly dispersed at tungsten grain boundaries as well as inside the tungsten grains.

Hence, APT can be converted to highly homogenous powder precursors of different compositions and fine scale morphologies. The precursors can be processed further into nanosized composite powders and sintered to highly uniform tungsten composites with fine microstructures. A much higher degree of powder uniformity and purity can be obtained as compared to methods based on mechanical mixing. Further, co-precipitation also offers the possibility to manipulate and control the size and shape of the precursor particles, to a higher degree than in alternative chemical processing methods such as spray drying.
5 Future Work

The materials' properties are a function of the different processing steps from the extraction of tungsten from the ore, to sintering of the final tungsten-based composite (Fig. 1.4). Further optimization of the materials should involve each of these steps to improve powder characteristics as well as the microstructure and the properties of the composite. Nevertheless, there are three interrelated aspects which can be regarded as more critical than others:

5.1 Processing of Powder Precursors into Phase Pure WC-Co or W-Y_2O_3:

W and Co containing precursors are relatively easy reduced to nano-sized W-Co composite powders. However, successful carburization to nano-scale WC-Co powders in carbon containing atmospheres requires optimization of gas composition and temperature. The carbon activity should be controlled to result in stoichiometric WC, without free C.

The reduction of rare earth doped tungsten precursors requires further attention in order to ensure a complete conversion of e.g. WO_3-Y_2O_3 mixed oxides to W-Y_2O_3 composite powders.

5.2 Evaluation of the Mechanical Properties of Nanocomposites

The mechanical properties of the fabricated materials must be evaluated using standards methods for testing of e.g. fracture toughness. This requires sintering of larger amounts of nanocomposite powders (200-300 g) by SPS and/or HIP.

5.3 Up-Scaling of Powder Precursors Reduction

The reduction of tungsten oxides in hydrogen atmosphere are known to be strongly influenced by the humidity within the powder bed (1.4.2 and 3.2.1.3). Water produced in the reaction, effects both nucleation and growth rates of the tungsten grains. An increase of the amount of precursor being reduced, increases the powder bed’s resistance to water transport and therefore also the humidity in the bed. Up-scaling of the reduction step will affect the reaction times and the final size of tungsten grains and requires optimization of processing parameters such as temperature, time and gas flow rate.
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7 References


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