Demonstration of Production of Tungsten Metal Powder and its Consolidation into Shapes

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Tungsten is a strategically important metal used as plasma facing component in fusion reactors, radiation shields in cancer therapy machines, ammunition in defence applications, high speed cutting tools etc. The primary resources or minerals occurring in India contain a very low value (0.25-0.5 wt. %) of tungsten. Mineral beneficiation processes involving crushing, grinding, primary and secondary gravity separation, floatation are essential to produce the ore-concentrate suitable for further processing up to the preparation of the intermediate ammonium para-tungstate (APT). APT was further converted to tungsten tri-oxide (WO$_3$). Hydrogen reduction of WO$_3$, producing high purity W metal powder was demonstrated in large scale batches. Densification of W powder was further studied using vacuum hot pressing at 1950°C, and high density W metal plates of 5 mm thickness and 60 mm diameter were produced. The products obtained at every stage were systematically characterized using X-Ray diffraction (XRD), scanning electron microscope (SEM), energy dispersive spectroscopy (EDS) and electron backscattered diffraction (EBSD) techniques.

Keywords: Tungsten, Hydrogen reduction, Hot pressing, Radiation shields

**Introduction**

Tungsten possesses high melting point (3410°C), high density (19.26 g/cc) and superior mechanical strength at high temperature. Tungsten metal is therefore being used as plasma facing components for instance diverter plates of fusion reactor (ITER), and as ammunition materials in military applications. Tungsten based heavy alloys such as W-Ni-Fe and W-Ni-Cu possess distinguished properties combined with their ability to absorb radiation as well as their outstanding mechanical properties and machinability. These are the ideal materials for a wide range of applications, such as in aerospace, the automotive industry, medical engineering and the construction industry. Different shapes of W-Cu alloys are used as gamma radiation shielding in the cancer therapy machines such as Bhabhatron. Tungsten is also used in cutting tools (cemented carbide tools), high speed steels and different grades of steels such as ferritic martensitic steels etc. Tungsten is therefore a strategically important metal for India.

However, all the ore deposits of tungsten present in India are of low grade compared to world resources. In India, the major deposits of tungsten are (i) Degana, comprising of four distinct types, namely, quartz vein, eluvial, phyllite and granite, (ii) Balda, (iii) Khobna-Kuki-Agargoan, (iv) Burugubanda-Tapaskonda, (v) Scheelite-bearing gold ores of Kolar and Hutti, and (vi) Madurai [1]. Total reserves of tungsten in the country are 50.22 M.T. [2]. However, the available grades of ores analyse between 0.04 to 0.5% WO$_3$ and most of the grade falls below 0.1% WO$_3$ [1]. The concentrate for commercial use generally needs 60-70% WO$_3$, requiring an enrichment of WO$_3$, between 300 to 1600 times. Even after such enrichment by physical beneficiation methods, the end product does not meet the desired specification in terms of purity and grade, because most of the tungsten minerals are found to be intimately mixed with undesirable elements like tin, molybdenum, phosphorus, arsenic, sulphur and other base metals. As regards processing, it has been found more profitable to produce low grade concentrates with higher recovery of tungsten from the lean ores. When such low grade concentrate is converted to an intermediate product such as ammonium paratungstate (APT), better plant economy results [1]. Therefore, an appropriate technology involving conversion of low grade concentrate to APT by aqueous processing is being developed to suit the Indian conditions, where, by and large deposits are of low grade in nature. In the present paper, a techno-economic scheme for processing of low grade tungsten ores as well as secondary resources is addressed. Hydrogen reduction of WO$_3$ has been demonstrated in kg scale batches. Pure tungsten metal powder produced by hydrogen reduction was further characterized using XRD and SEM. Finally, the fabrication of tungsten shapes was done using vacuum hot pressing, and the consolidated product was characterized using various techniques.

**Processing of low grade wolframite concentrate**

In India, tungsten minerals-wolframite and scheelite occur in many places but in very low concentration. One of the largest deposits of wolframite, located at Degana, Nagaur district of Rajasthan. Wolframite is the main tungsten mineral associated with other minerals like quartz, mica, feldspar, sulfide and topaz. Physical beneficiation treatment comprises crushing, grinding, primary and secondary gravity separation, floatation yields two types of concentrates-one assaying 7-30% and the other about 65% WO$_3$ [1]. The concentrate with higher values of WO$_3$ is amenable to further economical recovery of tungsten. The flow sheet for low-grade wolframite concentrate was developed earlier at BARC [3] with the objective of recovery of tungsten and other valuable associates.
Processing of secondary resources

In the manufacture of cemented carbide tools, besides main ingredients WC and the binder Co, various other carbides such as NbC, TaC and TiC etc. are incorporated, in varying proportions either individually or in different combination to attain specific combination of metallurgical properties. WC tools scrap is another indigenous source of tungsten. Recycling of cemented carbide tools scrap aimed at recovery of W and Co metals, generates residue sludge containing substantial quantities of W, Co, Nb and Ta. WC scrap and corresponding sludge, generated on recycling of scrap for recovery of W and Co therefore differ in chemistry from batch to batch. Flow sheets for processing of different types of carbide sludge were developed at BARC [4].

Recovery of pure tungsten tri-oxide (WO₃)

Once the tungsten values are brought into solution, it is then subjected to purification. Purification is accomplished by first, converting the entire W into hexavalent state using an oxidant such as HNO₃/NaNO₃, and then adjusting the pH of the solution to alkaline range of 10.5-11 in order to cause precipitation of silica, alumina and iron. The clarified solution after filtration is then purified by three different routes namely (1) precipitation as synthetic scheelite, (2) recrystallisation as ammonium paratungstate (APT) and (3) carbon adsorption and desorption. Finally, WO₃ is obtained by calcination of APT. High purity WO₃ required for conversion to W metal powder is produced from APT.

Preparation of W by hydrogen reduction of WO₃ in kg scale

Tungsten metal powder was produced by hydrogen reduction of tungsten tri-oxide at 900-1000°C. Hydrogen reduction of WO₃ to metallic tungsten takes place in number of steps:

\[
\text{WO}_3 \rightarrow \text{WO}_{3.7} \rightarrow \text{WO}_{2.9} \rightarrow \text{WO}_2 \rightarrow \text{W}
\]

The overall reaction is

\[
\text{WO}_3 (s) + 3\text{H}_2 (g) \rightarrow \text{W} (s) + 3\text{H}_2\text{O} (g)
\]

Thermogravimetric (TG) studies were conducted for hydrogen reduction of WO₃, presented in Fig. 1. Thermogravimetric analysis (TGA) plot shown in Fig. 1 clearly indicates the stepwise reduction of WO₃ to pure W.

The hydrogen reduction reactions are reversible in nature and their course is determined by the equilibrium constants:

\[
K_p = \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}}
\]  

Where, \( P_{\text{H}_2\text{O}} \) is the equilibrium partial pressure of water vapour and \( P_{\text{H}_2} \) the equilibrium partial pressure of hydrogen.

The stability of oxides and tungsten was predicted with reduction temperature and moisture content of the flowing gas [5].

Preparation of pure W from WO₃ by hydrogen reduction was carried out using a static bed in tubular type resistance heating furnaces. Initially, the hydrogen reduction was carried out in 50 g scale, and the parameters of the reduction process were optimized. Subsequently, a larger scale reduction facility was designed and fabricated in-house. The parameters of hydrogen reduction such as temperature, hydrogen flow rate, time, powder bed thickness are optimised systematically to achieve 100% yield of hydrogen reduction of WO₃. Fig. 2 represents the pure W metal powder produced after hydrogen reduction of 1 kg of WO₃. The as-reduced powder was further characterized using SEM and XRD.

The SEM image (Fig. 3) of the W metal powder was captured. The average particle size of individual W powder varied between 5 to 10 µm.

Fig. 1: TG plot for hydrogen reduction of tungsten tri-oxide

Fig. 2: Tungsten metal powder produced by hydrogen reduction of 1 kg of WO₃

Fig. 3: SEM image showing the individual W powder produced by hydrogen reduction
XRD analysis (Fig. 4) confirmed the formation of only W phase in the product powder.

Consolidation of W powder into shapes

Due to higher melting temperature, the consolidation of tungsten into high density products is a challenging task. In the current investigation, the vacuum hot pressing technique was adopted to study the densification behaviour of pure W. The powder prepared by hydrogen reduction was filled in a graphite die and hot pressing was done using graphite plunger at 1950°C for 2 h by applying the progressive load up to 50 ton. The density of the hot pressed W was found to be about 18.2 g/cc. Applying optimized processing parameters, the W shapes of 60mm diameter and 5 mm thickness (Fig. 5a) were produced by hot pressing. Fig. 5(b) shows a 40 mm × 40 mm × 4 mm plate prepared from hot-pressed plate after EDM cutting and subsequent machining.

The as-consolidated tungsten was characterized with respect to hardness measurement, and microstructural analysis using SEM and EBSD. The average Vickers hardness of the hot-pressed W was found to be 305 HV at 500 g load. For EBSD studies, the samples were cut from the hot-pressed plates using EDM and polished up to 0.5 µm diamond finish followed by electrolytic polishing using 2% NaOH aqueous solution. Figs. 6 and 7 represents the EBSD maps obtained from the EP surface of the samples taken respectively from the
directions perpendicular and parallel to the applied load during hot pressing. Polycrystalline tungsten has been formed, and the average grain size is about 10-15 µm (Fig. 6) in perpendicular direction and 6-8 µm (Fig. 7) in the direction of parallel to the applied load. The microstructure of the hot pressed W consisted of recrystallized grains and the orientations of the grains are found to be random (Figs. 6b and 7b).

Summary

Hydrogen reduction of tungsten tri-oxide in kilogram scale batches was successfully demonstrated. Pure tungsten metal powder of particle size about 5-10 µm was produced. Densification behaviour of tungsten powder was studied, and high density tungsten metal plates of 5mm thickness were successfully fabricated by vacuum hot pressing at 1950°C. Further work will be continued to produce tungsten tri-oxide from low grade scheelite-bearing gold ores of Hutti and Kolar. This technology is now available from BARC for large scale production of W powder.

Fabrication of different shapes of W based alloys (W-Cu and W-Ni-Fe) required for Bhabhatron is currently being taken up at BARC.

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References: