

Investigation of the Larger Scale Tungsten Production by the Electrochemical Reduction Technique

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Abstract

Hydrogen reduction of WO_3 is the major industrial process in tungsten production. A promising cost and energy efficient method was recently reported [1-3] for direct electrochemical production of tungsten from $CaWO_4$ (scheelite) which is estimated as the two third of the all tungsten reserves of the world. Following the above mentioned patent, several studies verified the production of metallic tungsten by electrochemical reduction of calcium tungstate in the laboratory. This study investigates the application of electrochemical reduction technique to produce larger amount of metallic tungsten as compared to laboratory experiments. The electrolyte was composed of calcium chloride and sodium chloride salts at eutectic composition (48 % mol NaCl at 873 K). The reduced samples were cleaned with dilute hydrochloric acid solutions and characterized by XRD and SEM. Examination of the results revealed that there are several problems against pilot-scale production, the biggest of which was observed as the electronic conduction provided by the graphite powders dispersed in the molten salt.

1. Introduction

Besides having the highest melting point ($3422+15^\circ\text{C}$) among all metals, tungsten also has very high thermal creep resistance, good high-temperature mechanical properties, high density, very low thermal expansion coefficient, very high moduli of compression and elasticity and good conductivity for electricity and heat [4]. Having these significant properties makes tungsten crucial in many technological applications. Main usage of tungsten is revealed in the production of cemented

carbides that have high hardness and enables shaping of diverse kind of materials. The other uses of tungsten are mainly in chemical applications such as catalysts, paints and lubricants. In addition, superalloys and tungsten heavy metal alloys contain tungsten due to its outstanding properties [5].

Despite there are more than thirty known tungsten minerals, only scheelite ($CaWO_4$) and wolframite ($(Fe, Mn)WO_4$) are industrially notable. Among all tungsten minerals, scheelite is the most abundant mineral of tungsten and its occurrence is approximately two third of all known tungsten deposits [6]. Tungsten production is carried through the hydrogen reduction of tungsten oxides in the temperature range 600 to 1000°C . Tungsten oxides are supplied from abovementioned minerals by converting via alkaline dissolution processes. There are several restrictions and difficulties encountered in converting scheelite into tungsten oxides. Therefore, scheelite is not the primary selection for the industrial use although it has much more deposits than wolframite minerals.

There is an alternative tungsten production method recently reported [1-3]. This method claims the electrochemical reduction of pelletized 2.5 grams of $CaWO_4$ to produce tungsten by using a eutectic NaCl– $CaCl_2$ electrolyte at 873 K. The end product was the mixture of metallic tungsten powder and calcium compounds [9]. Several studies [7-9] indicated that production of tungsten by electrochemical reduction of calcium tungstate is feasible and energy efficient in the laboratory scale experiments. This study was conducted to investigate the successful alternative tungsten powder

production route employing electrochemical reduction of calcium tungstate to larger scale.

2. Experimental Procedure

A pilot-scale tungsten production line was designed and manufactured with the capacity of 300 g tungsten production per day. The external dimensions of the furnace were 500 mm diameter and 500 mm height. It had three rows of resistance wires at the side walls and one row at the bottom. By this way, it became possible to heat the furnace by the resistances positioned at the side walls or at the bottom alone or using both of the resistances

A stainless steel (AISI 316 Ti) vessel was placed into the furnace to contain the salt bath. It had 360 mm outer diameter, 4 mm thickness and 360 mm height. The CaWO_4 (Noah, 18418) powder was introduced to the molten salt within a stainless steel current collector as the target temperature of 600°C was reached.

Two different graphite anodes were used. While one of them was 100 mm diameter rod used initially, the other was an Al_2O_3 coated graphite rod of 100 mm diameter used in latter experiments. In order to arrange the position of the graphite rod vertically, an elevator system was placed next to the furnace. An AC electric motor and a redactor were used to rotate the screw at low speed to modify the anode in the up and down direction. The system carrying the arm was insulated with the help of castermid to supply electrical current directly to anode.

The industrial grade CaCl_2 (Solvay) and NaCl (Ucleroğlu) salts were mixed to obtain a salt solution of eutectic composition as the electrolyte. Melting of the salt mixture was completed in 48 hours and most of the H_2O from hydrated CaCl_2 was removed at low temperatures. Argon gas flow was provided during heating to aid dehydration. In the experiments, about 20 kg of salt mixture consisting of 12,78 kg CaCl_2 and 7,22 kg NaCl was placed into the bath so as to provide 10 cm electrolyte depth. The CaCl_2 salt contained 2 moles of H_2O per mole; therefore, 17 kg of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ was used at the beginning. The CaCl_2 was dehydrated after 4,16 kg of H_2O was removed during heating. The CaWO_4 powder, weighing 100 to 300 gr, was placed onto the stainless steel cathode current collector and dipped into the electrolyte, as the temperature reached the target temperature of 600°C.

The graphite rod was also interacted into the electrolyte and the process was initiated by application of a potential difference of 3 V between the cathode and the anode. This potential difference was large enough to reduce

CaWO_4 without continuous electrolysis of the components forming the electrolyte as indicated in previous studies [1,7-9]. The experiment durations were varied from about 8 to 18 hours.

After the experiments, produced powder was washed with tap water to separate the solidified salt around it so that it could be taken out of the current collector. It was subsequently treated with 5 liters of a 0.2 M HCl solution for 30 minutes and pulp was formed. The pulp was filtered under vacuum and dried at room temperature to obtain the reduced powder.

3. Results and Discussion

As the stainless steel current collector that contained CaWO_4 powder interacted with molten salt, formation of bubbles was observed on the surface of the electrolyte. The EDX analysis of the CaWO_4 the powder indicated the presence of 1.48 % wt. Na in the raw material as can be seen in Table 1.

Table 1. EDX analysis of the CaWO_4 (Noah, 18418) powder.

Element	Wt %	At %	K-Ratio	Z	A	F
O K	23,52	68,87	0,0106	1,1432	0,1430	1,0000
Na K	1,48	2,84	0,0032	1,0730	0,2133	1,0002
Ca K	14,92	16,67	0,0818	1,1115	0,5113	1,0052
W L	60,08	14,62	0,5107	0,8434	1,0511	1,0000
Total	100	100				

The presence of Na was most probably considered due to residues from soda roasting and leaching steps. Powder was cleaned in 0.1 M HCl solution to eliminate the formation of bubbles when it was introduced to molten salt. The EDX analysis after HCl treatment and drying at 200°C showed that Na was completely removed as can be seen in Table 2.

Table 2. EDX analysis of the CaWO_4 (Noah, 18418) powder after HCl washing.

Element	Wt %	At %	K-Ratio	Z	A	F
O K	23,24	67,49	0,0352	1,1424	0,1418	1,0000
Ca K	14,44	16,76	0,0775	1,1108	0,5140	1,0052
W L	62,28	15,75	0,5160	0,8429	1,0515	1,0000
Total	100	100				

The typical XRD result of the reduced powder after one of the experiments is given in Figure 1. To remove the calcium byproducts; Ca(OH)_2 and/or CaCO_3 , the reduced powder was cleaned by a dilute HCl solution as explained in the experimental procedure. As can be seen in this figure, tungsten could be produced but the reduction was not complete. Presence of Ca(OH)_2 was because of the incomplete leaching by HCl and can be eliminated by increasing the treatment duration.

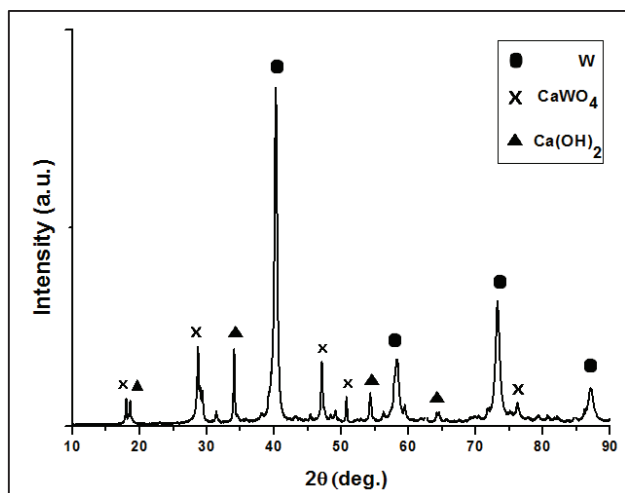


Figure 1. XRD Pattern of the reduced sample, obtained from the cell employing graphite anode without alumina cover, treated with 0.2 M HCl

In addition to incomplete reduction of CaWO_4 , there were other problems related to the materials used in the construction of the cell.

The current-time graph of the experiments was recorded with a self-developed computer software. The graph indicated that the efficiency was very low when compared to the laboratory scale experiments. The problem was most probably due to the oxidation of graphite anode inside the furnace above the electrolyte level. By this way, it is considered that graphite powders were dispersed in the molten salt and caused electronic conduction. The slow rate of electrochemical reduction could not produce large volumes of CO_2 and or CO to provide positive pressure inside the cell which could prevent air penetration into the system. The photograph of the graphite rod (Figure 2) after electrolysis demonstrated the abrasion present specifically at around the contact zone of graphite with the electrolyte.



Figure 2. The graphite anode without alumina cover used in the early experiments

In the light of above findings, the setup was redesigned to overcome the problems encountered in the production experiments.

For this purpose, an alumina coated graphite was replaced the former one. Coating was applied to the outer surfaces of the graphite that is not in contact with molten salt. Furthermore, the whole experiment was conducted under continuous flow of argon gas to provide a reducing atmosphere in the cell and prevent air penetration.

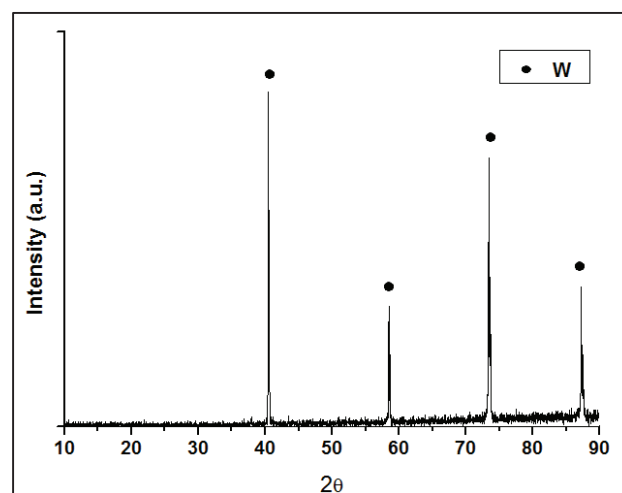


Figure 3. XRD Pattern of the reduced sample, obtained from the cell employing graphite anode employing alumina cover, treated with 0.2 M HCl

This modification provided considerable reduction in the oxidation of graphite. XRD Pattern indicated the reduction of CaWO_4 to tungsten were succeeded. All the characteristic peaks of tungsten were detected on XRD pattern. The particle size of the electrochemically produced W powder is less than 1μ as can be seen in Figure 4. Particle size analyses of this powder could not

be performed due to agglomeration. Because the particle size is small, the particles have high surface energies and high tendencies to agglomerate.

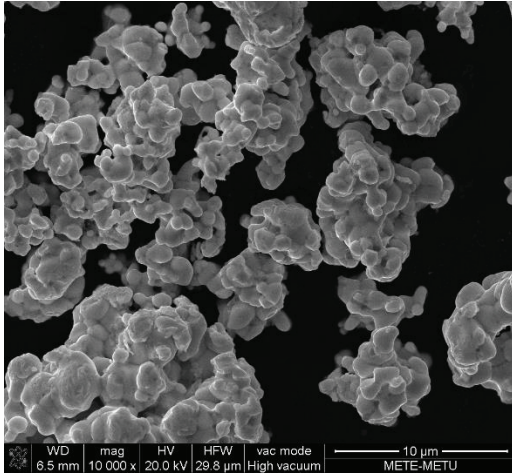


Figure 4. SEM Image of the electrochemically reduced sample

4. Conclusion

The larger scale electrochemical reduction of CaWO_4 in eutectic molten salt medium ($\text{CaCl}_2\text{-NaCl}$) at 600°C was investigated. The efficiency of the process was not as successful as laboratory scale studies [7-9]. The modifications in the graphite anode and furnace design eliminated some of the problems encountered. Furthermore, the results were promising in terms of economic feasibility and energy efficiency to further investigation of the present route.

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