Studies on the preparation of pure ammonium para tungstate from tungsten alloy scrap ☆

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Abstract

Ammonium paratungstate was prepared from tungsten alloy swarf employing anodic dissolution in sodium hydroxide using a packed bed configuration followed by chemical conversion into ammonium tungstate through tungstic acid. The alkaline tungstate solution was dialysed to recover sodium hydroxide, which could be recycled to the electrolytic dissolution. The influence of anodic current density and other parameters on dissolution/recovery was studied and discussed. It was observed that a current density of 600 mA/100 g scrap could be applied when the concentration of NaOH was maintained around 2.5 M. The energy consumption for anodic dissolution was 2.14 kWh/kg W with more than 90% recovery achieved. XRD studies indicated that the exhausted scrap contained an alloy of nickel and iron with a very low percentage of tungsten. APT sample prepared through anodic dissolution in NaOH was characterized.
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1. Introduction

Tungsten is one of the most highly refractory metals and finds extensive applications such as incandescent lamp filaments, heating elements in high temperature furnaces, electronic heaters, X-ray emission tubes, TIG welding electrodes etc. The metal is structurally useful because of its very high strength to weight ratio above 1370 °C.

Tungsten in the form of alloys and carbides is largely employed in tool industry and also in defence.

Ammonium paratungstate (APT) is the intermediate product for the preparation of either tungsten or tungsten carbide or tungsten based materials. APT is a highly crystalline, colourless and water insoluble compound with chemical formula $(NH_4)_2H_2W_{12}O_{42}.4H_2O$ and hence could be prepared free from impurities.

The conventional route to APT is to digest the ore or oxidized scrap in concentrated alkali under high temperature. It is then subjected to chemical methods for the removal of impurities like iron, silica, magnesium and finally tungstic acid is prepared through the formation of calcium tungstate. The compound thus prepared is dissolved in ammonia to form ammonium

tungstate. The solution is evaporated and APT is crystallized under optimized conditions (Shamsuddin and Sohn, 1981).

In the present study, an attempt has been made to prepare APT from tungsten alloy employing anodic dissolution followed by electrodialysis, molybdenum removal, tungstic acid precipitation, dissolution in ammonia and crystallization. The APT was characterised and compared with that of the commercial one.

2. Experimental procedure

The alloy used was made by mixing W, Mo, Fe and Ni powders heating at about 1300 °C in the presence of hydrogen and finally annealed in vacuum at around 1000 °C. The resultant alloy was composed of tungsten particles cemented within an alloy matrix of nickel and iron. Tungsten alloy scrap in the form of turnings was employed for all the experiments. The scrap was cleaned to remove all dirt, oil etc. and then used. The composition of the fresh scrap was W−88%, Ni−7.5%, Fe−4%, Mo−0.3%, while that of once leached scrap was around 74.6%.

2.1. Galvanostatic experiments

For anodic potential measurements the electrolytic cell set up consisted of a perforated PVC anode basket (dia 5 cm) packed with the scrap with a graphite rod as the current lead and a stainless steel (SS) sheet cathode of size 5 cm×8 cm within a 500 mL beaker. The electrolyte employed was NaOH with and without additive, viz. chloride.

The longer duration experiments were carried out in a similar set up, but larger in size. A cylindrical PVC tank (20 cm dia×30 cm height) having provision for inlet and outlet served as electrolytic cell. The anode
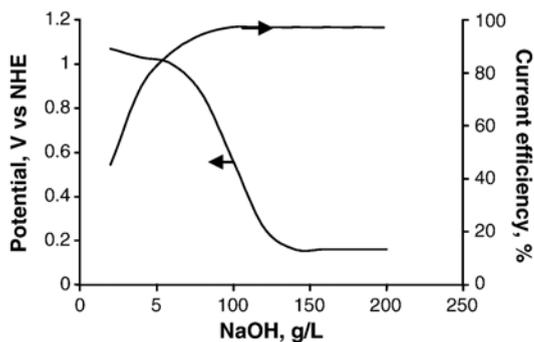
Fig. 1. Effect of concentration of sodium hydroxide on anode potential and current efficiency at 30 °C, current density 600 mA/100 g scrap.
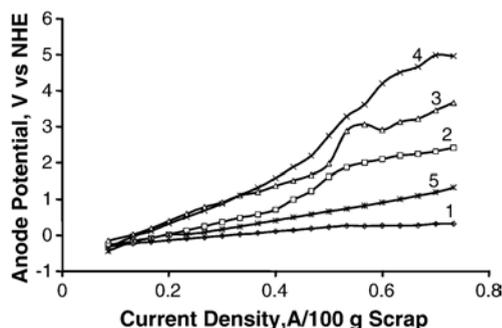
Fig. 2. Relationship between current and anode potential under different conditions. 1. Fresh scrap in 100 g/L NaOH. 2. Fresh scrap in 100 g/L NaOH containing 10 g/L NaCl. 3. Fresh scrap in 100 g/L Na_2WO_4 + 60 g/L NaOH. 4. Partly leached scrap in 100 g/L Na_2WO_4 + 60 g/L NaOH. 5. Partly leached scrap in 100 g/L NaOH.

consisted of a perforated PVC cylinder packed with the scrap with a cylindrical graphite rod used as current lead, a SS sheet cathode was placed adjacent to the anode.

For continuous runs, fresh sodium hydroxide was fed from an overhead tank and the outlet containing sodium tungstate and sodium hydroxide was collected. The flow rate was adjusted so as to maintain 100 g/L Na_2WO_4 with 60 g/L NaOH in the electrolytic cell.

Sodium hydroxide was regenerated employing a two compartment cell separated by Nafion (400 series) cation exchange membrane with SS cathode and catalytic oxides coated titanium anode.

2.2. Potentiodynamic studies–influence of additives

Cleaned tungsten alloy scrap with an exposed geometrical surface area of 0.3 cm^2 was used for the experiments in an H-type cell. Platinum gauze was employed as counter electrode. Potentials were measured vs. saturated calomel electrode (SCE) through a Luggin capillary and converted to NHE.

2.3. Preparation of Ammonium Para Tungstate (APT)

The sodium tungstate solution was subjected to molybdenum removal step employing sodium hydrogen sulphide as described elsewhere (Lassner, 1995). The pH of the solution was adjusted suitably, tungstic acid was precipitated under optimum conditions and APT was prepared.

All the chemicals employed in small scale experiments were of analytical grade. The measurements were carried out at ambient temperature.

3. Results and discussion

3.1. Galvanostatic studies

3.1.1. Influence of concentration of electrolyte

Fig. 1 presents the effect of the concentration of sodium hydroxide electrolyte on anode potential and current efficiency. The anode potential decreased slowly up to 60 g/L, steeply till 140 g/L and remained constant thereafter. The current efficiency for tungsten dissolution remained essentially 100% above 100 g/L and it was only 40% at a concentration of 20 g/L NaOH.

In case of sodium hydroxide electrolyte, the following three anodic reactions are likely to happen (Latimer, 1952).

$$4OH^- \rightarrow O_2 + 2H_2O + 4e \qquad + 0.401V \qquad (1)$$

$$W + 8OH^- \rightarrow WO_4^{2-} + 4H_2O + 6e \qquad -1.05V \quad (2)$$

$$Mo + 8OH^- \rightarrow MoO_4^{2-} + 4H_2O + 6e \qquad -1.05V \quad (3)$$
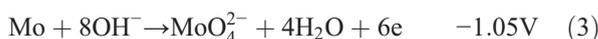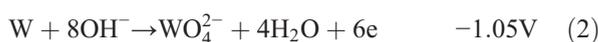
At very low concentration, the predominant reaction is oxygen evolution according to the anodic reaction (1). At a concentration above 60 g/L, reactions (2) and (3) are taking place. The other elements in the alloy, Fe and Ni do not take part in dissolution. Above 140 g/L the anode potential remained more or less constant indicating that 100% dissolution is taking place. Further, the solution is highly conductive and hence iR drop is negligible.

3.1.2. Influence of anode current density

The relationship between current density and anode potential in different alkaline electrolytes employing either fresh or partly leached scrap keeping other electrolytic parameters constant is depicted in Fig. 2.

In general, it could be understood that the anodic reaction depends on the free concentration of sodium hydroxide as well as the composition of the scrap. Fresh

Table 1
Influence of addition of NaCl to NaOH on the flade and gas evolution potential

Electrolyte	Flade		Gas evolution	
	Potential, V vs NHE	Current density A/cm^2	Potential, V vs NHE	Current density A/cm^2
NaOH	0.194	0.200	0.746	0.153
NaOH+ 10 g/L NaCl	0.153	0.169	0.702	0.107
NaOH+ 50 g/L NaCl	0.109	0.138	0.683	0.085
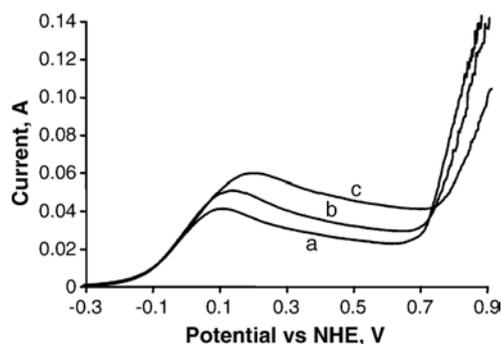
Fig. 3. Potentiodynamic behaviour of tungsten alloy in (a) 100 g/L NaOH+50 g/L NaCl, (b) 100 g/L NaOH+10 g/L NaCl, (c) 100 g/L NaOH, scan rate 5 mV/sec.

scrap (∼ 90% W) exhibits a linear increase in 100 g/L sodium hydroxide electrolyte with minimum rise of overpotential with increase in current density (curve 1), while the partly leached scrap (∼ 70–75% W) exhibited the same trend with a slightly higher slope (curve 5).

The addition of NaCl (10 g/L) in the electrolyte increases the slope and above 400 mA/100 g current density the curve deviates from the straight line (curve 2). The slopes of the other two (curves 3 and 4) are still higher when the electrolyte contained 100 g/L Na$_2$WO$_4$ and 60 g/L NaOH. In case of curves 3 and 4 the deviation from smooth line is due to disturbances caused by gas evolution.

It appears that when free sodium hydroxide is 100 g/L the dissolution occurs with ease. When free alkali is reduced the dissolution is retarded. Regarding the influence of chloride, the curve deviates from the straight line above a specific current density, may be due to shift in flade potential to the negative side.

The formation of hypochlorite ion, is also a probable anodic reaction according to

$$2Cl^- + 2NaOH \rightarrow NaCl + NaOCl + H_2O$$
$$+ 2e \qquad + 0.89V \qquad (4)$$
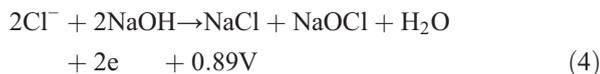
From the graph it could be inferred that one can safely apply a current density of 600 mA/100 g, when fresh scrap is employed.

3.2. Potentiodynamic studies

Fig. 3 and Table 1 present the electrochemical behaviour of the tungsten alloy in sodium hydroxide electrolyte with and without sodium chloride. When the alloy is subjected to anodic polarization, the active dissolution starts from −0.170 V vs. NHE and after reaching the flade potential film formation occurs

Table 2
Anodic dissolution of tungsten in sodium hydroxide

S. No.	Mass/ g	Condition (processed)	Current/ A	CE/ %	Energy kWh/kg	Initial bulk density g/cc
1	4144	Fresh	20	96	1.84	2.77
2	1281	Once	10	100	1.78	1.02
3	661	Twice	6	100	1.88	0.73
4	2834	Fresh	14	96	2.04	2.76
5	965	Once	7	95.9	2.15	0.99
6	438	Twice	3	63	2.75	0.57

Electrolyte concentration: free sodium hydroxide 60 g/L, sodium tungstate 100 g/L.

followed by oxygen evolution at around 0.750 V. Between 0.1 and 0.750 V the formation of different nonstoichiometric oxides occurs followed by stoichiometric WO_3 at around 0.75 V vs NHE (Ortiz et al., 1988a,b). The addition of sodium chloride to the electrolyte decreases the flade potential from 0.194 to 0.109 V. In addition, the gas evolution also shifts to lower potentials, viz. from 0.746 to 0.683 V.

The reason for the shift in the slope in case of curve 2 of Fig. 2 could be due to the formation of a passivating film earlier than in the absence of sodium chloride. Hence, dissolution is reduced in the presence of sodium chloride.

3.3. Anodic dissolution in NaOH – longer duration

The typical results of experiments are presented in Table 2.

It is evident that extraction of tungsten is possible with a current efficiency >90% for at least three successive runs. The current density applied mainly depends on the weight and composition of the scrap. When carefully controlled more than 90% of tungsten
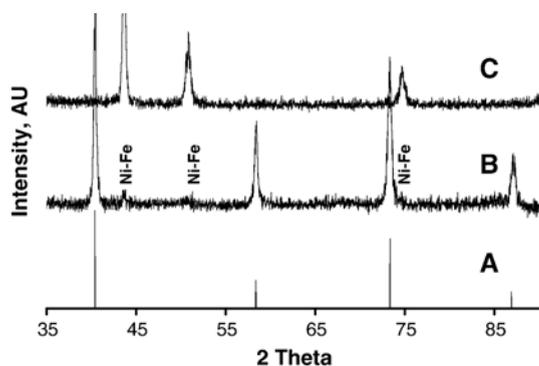
Fig. 4. X-ray diffraction patterns of fresh and processed tungsten scrap; standard values for tungsten (A), fresh scrap (B) and processed scrap (C).

Table 3
Data on electrodialysis experiment

Anolyte NaOH g/L		Catholyte NaOH g/L		Cell voltage/ V		Energy/ kWh	Interelectrode distance/cm
Initial	Final	Initial	Final	Initial	Final		
68	11.13	39.6	98.4	3.85	5.26	5.67	3

value could be brought into solution with minimum energy consumption. Current efficiency was low for the last experiment as the tungsten content was less as indicated by the low bulk density.

The table also indicates the decrease in bulk density with repeated processing. When fresh scrap is subjected to anodic dissolution (I time), the composition is reduced to ∼ 70% W with steep fall in bulk density from 2.8 to 1.00 g/cc. When the scrap is further subjected to anodic dissolution (II and III time), the composition reached a value of ∼ 20% W with bulk density ∼ 0.50. Further dissolution did not affect the bulk density (not indicated in the table).

3.4. X-ray diffraction studies

Fig. 4 shows the XRD patterns of both fresh and processed scraps along with standard of W, presented as strip chart for comparison. It clearly indicates that all the four predominant peaks of tungsten are exhibited in the XRD pattern of fresh scrap along with a feeble peak of nickel–iron alloy. XRD pattern of used scrap indicates the predominance of nickel–iron alloy with tungsten.

3.5. Electrodialysis

The sodium tungstate solution obtained by anodic dissolution contains 0.5 to 0.75 M of sodium tungstate and 1.5 M of sodium hydroxide. The major portion of free sodium hydroxide was separated by electrodialysis so as to reduce the consumption of hydrochloric acid used for neutralization in the later stage of the process. The sodium hydroxide generated was reused for anodic dissolution. Table 3 presents the typical data obtained in one such experiment.

Table 4
Chemical Composition of APT

Sample	WO_3	Fe	Mo	Cu	Ni
	%	%	%	%	%
Commercial APT	88–90	0.005	0.01	Nil	Nil
Prepared through NaOH	90	0.001	0.016	0.001	Nil

Electrical energy consumption for producing NaOH in this process is higher than that achieved in NaCl electrolysis (2.25 kWh/kg NaOH) in modern membrane cells. The energy could be reduced if cascading system and hydrogen consuming anode are employed as in the case of sodium sulphate electrolysis (Jorissen and Simmrock, 1991).

3.6. Preparation of ammonium paratungstate

Table 4 presents the chemical composition of APT prepared through anodic dissolution in sodium hydroxide, followed by molybdenum removal and tungstic acid precipitation, in comparison with commercially available APT.

It could be inferred that APT prepared via sodium hydroxide is almost at par with the commercial APT.

X-ray diffraction patterns of the APT prepared from the scrap showed it was essentially identical to commercial APT tetrahydrate.

4. Conclusions

Anodic dissolution could advantageously be employed for dissolving tungsten from tungsten alloy scrap. The energy consumption for dissolution in NaOH electrolyte is approx. 2 kWh/kg. The addition of NaCl to NaOH electrolyte is not advantageous in the dissolution. Recycling of NaOH obtained through electrodialysis is possible.

The APT prepared was of commercially acceptable quality.

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