17ᵗʰ INTERNATIONAL CONFERENCE on NON-FERROUS MINERALS & METALS-2013

With Satellite Session on :
Harnessing of natural non-ferrous mineral resources

July 5-6, 2013

Chanakya BNR Hotel
Ranchi, India

Organised by :
Cm Corporate Monitor
In association with :

MECON LIMITED
&
Al Circle Alcircle

17th International Conference on Non-ferrous Minerals & Metals-2013

Organised by:

Corporate Monitor *Cm*

In association with:

MECON LIMITED

&

Alcircle

Sponsored by:

नालको **NALCO** & हिन्दुस्तान कॉपर लिमिटेड **Hindustan Copper Limited**

Supported by:

ALSTOM & **JIWANRAM SHEODUTTRAI GROUP**

Inaugural Tea Sponsored by:

HIMADRI CHEMICALS & INDUSTRIES LIMITED

REDUCTION OF AMMONIUM PARATUNGSTATE GENERATED DURING HYDROMETALLURGICAL PROCESSING OF TUNGSTEN - COPPER (W-CU) BORINGS

Manoj Kumar[1*], D. C. Sau[1], P. Nishant[2], M. Bhattacharya[1]

[1]MEF Division, CSIR-National Metallurgical Laboratory, Jamshedpur
[2]Chemical Engg. Department, Manipal Institute of Technology, Manipal

Abstract

Tungsten-copper (W-Cu) alloy is employed for manufacturing heavy duty contactors, relays, switches etc. During production of such components, W-Cu turnings/borings are generated. At CSIR-NML, a process for recovering tungsten and copper from tungsten-copper borings containing 46.01% W, 53.78% Cu, 0.13% Fe and other minor metals as high purity tungsten powder and copper powder has been developed. In the present work, the detailed investigation on reduction of ammonium paratungstate (APT) having purity 99.95% by hydrogen gas to produce the high purity tungsten powder was presented. The various process parameters such as temperature, time and flow rate of hydrogen gas were optimized. At the temperature of 800^0C and 0.1 lpm flow rate a reduction of 77.78% was observed up to 2h time. At 900^0C, with increase in flow rate from 0.1 lpm to 0.3 lpm the increase in reduction was found to be from 63.88% to 99.99% at 1h time. At still high temperature of 1000^0C, almost complete reduction was obtained at 0.1 lpm flow rate in 1h time. The effect of bed-depth was also carried out. At all temperatures chemical reaction and nucleation control were the rates determining steps.

1. Introduction

Ammonium paratungstate (APT) is the intermediate product generated during the recovery of tungsten from the tungsten-copper borings. In this work, the APT was directly reduced to produce the tungsten using the hydrogen gas. Bhosale et al.[1] have reported that the blue or yellow tungsten oxide, the intermediates generated by the heating of ammonium paratungstate, is loaded in corrosion resistant steel boats, and then it is reduced under hydrogen to metallic tungsten. They were used a pusher type furnace to reduce the tungsten oxide, wherein a boat is progressively pushed into the tube of the furnace, travelling through the hot zone under a flow of hydrogen in which particle size of the product was controlled by the temperature of the furnace, flow and moisture content of hydrogen, rate of the travel of the boat, etc. The special concern to this work is the direct reduction of ammonium paratungstate in a tubular furnace. The APT generated during the processing of W-Cu borings had the purity of 99.95%, which was used as the starting material for the reduction of APT. In this work, the influence of temperature, flow rate of hydrogen gas, time on reduction and bed depth of ammonium paratungstate (APT) to produce the tungsten powder have been discussed. The kinetics of reduction of tungsten oxide has also been proposed.

2. Theoretical Details

The reactions taking place during reduction are as follows:

$$4 WO_3 + H_2 = W_4O_{11} + H_2O$$

$$1/3\ W_4O_{11} + H_2 = 4/3\ WO_2 + H_2O$$

$$1/2\ WO_2 + H_2 = 1/2\ W + H_2O$$
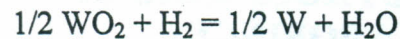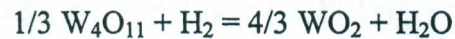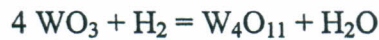
At lower temperatures (600°C) and lower moisture contents, the reduction proceeds by solid-state diffusion of the oxygen out of the oxide [2] and can be represented by the following principal chemical reaction:

$$WO_{3(g)} + 3H_{2(g)} \longrightarrow W_{(s)} + 3H_2O_{(g)}$$

Reduction of the oxide can be controlled by the temperature and the water vapour partial pressure. On complete reduction, an oxide-pseudomorphic[2] metal sponge is formed.

At higher temperatures, the reaction precedes stepwise via the oxides $W_{20}O_{58}$, $W_{18}O_{47}$ and WO_2 to tungsten metal. Only the first transformation to $W_{20}O_{58}$ and each nucleation of a newly formed phase on further reduction are solid-state reactions. All other transformations are linked to gas-phase of tungsten as the volatile oxide hydrate $WO_2(OH)_2$, and are associated with a significant change in the shape of the crystal faces. The formation of the vapour-phase oxide hydrate takes place by reaction of the corresponding sub-oxide with water formed in the reduction. The vapour pressure of the oxide-hydrate in equilibrium with a stable compound formed under the reaction conditions is lower than that in equilibrium with the continually decreasing amount of the unstable compound. As a result of these gradients, chemical vapour transport (CVT) takes place, so that the higher oxide decreases in quantity and the lower oxide increases [2]. The interphase reaction can plausibly be divided into three steps:

- Formation of $WO_2(OH)_2$ from the oxygen rich compound with H_2O
  $$WO_{2(s)} + 2H_2O_{(g)} \longrightarrow WO_2(OH)_{2(g)} + H_{2(g)}$$

- Transport of $WO_2\ (OH)_{2(g)}$ to the compound of lower oxygen content
- Reduction of $WO_2(OH)_{2(g)}$ by hydrogen at the surface of the compound of lower oxygen content (or the metal).

  $$WO_2(OH)_{2(g)} + H_2 \longrightarrow W_{(s)} + 3H_2O_{(g)}$$

Furnaces can be provided with several temperature zones controllable between 600-1100°C. The flow of hydrogen is usually in a counter-current direction, more rarely co-current to enhance the reaction rates, and a drying stage is always included in the circuit. The hydrogen acts not only as a reducing agent, but also carries away the water formed. The flow rate is therefore one of the parameters for controlling the water vapour partial pressure. Other control parameters are:

- The amount of oxide charged to the furnace per unit time
- The depth of the oxide bed
- The porosity of the oxide bed (particle size and particle size distribution)
- The moisture content of the hydrogen entering the furnace

- The porosity and depth of the bed, in conjunction with the hydrogen flow rate, determine the rate of diffusion of water vapor from the bed.

2.1 Basis of Reduction of Ammonium Paratungstate (APT)

Generally APT is not directly reduced to metal since its reduction produces large amounts of ammonia and water vapour. It is converted to tungsten oxide which is subsequently reduced to tungsten metal. In this work APT was directly reduced to metal powder. Steps are as follows:

Step 1: Removal of ammonia and crystallised water

Theoretical Data: 11.17 % loss in weight when heated above 450^0C [24].

Observation: When heated above 450^0C 11.5% loss in weight

Step 2: Reduction of tungsten oxide

$$WO_3 + 3H_2 \longrightarrow W + 3H_2O$$

Given: Wt. of the sample taken = 2 gm

APT is given by $(NH_4)_{10}[H_2W_{12}O_{42}].4H_2O$

At wt. of W = 183.85

At wt. of O = 16

Molecular wt. of WO_3 = 231.85

Molecular wt. of H_2O = 18

1. Upto 100^0C the material is dried and loses its four water molecules:
   $(NH_4)_{10}(H_2W_{12}O_{42}).4H_2O \longrightarrow (NH_4)_{10}(H_2W_{12}O_{42}) + 4H_2O$

   This corresponds to a weight loss of 2.30 %.

2. Between 100^0C and approximately 220^0C only NH_3 is evolved and amorphous ammonia meta tungstate (AMT) is formed:
   $(NH_4)_{10}(H_2W_{12}O_{42}) \longrightarrow (NH_4)_{10}(H_2W_{12}O_{42}).2H_2O + 4NH_3$

   This corresponds to a total weight loss of 4.47% .

3. Between 220^0C and 450^0C simultaneous loss of NH_3 and H_2O takes place and above 450^0C only WO_3 is left.

2.2 Kinetics of Reduction

The rate of reaction can be controlled by diffusion, chemical reaction or nucleation. The rate controlling steps are represented by following expressions [20]:

For diffusion control, (gas diffusion through product layer)

$$1-3(1-X)^{2/3} + 2(1-X) = kt$$

For Chemical reaction control,

$$1-(1-X)^{1/3} = kt$$

For nucleation control,

$$-\ln(1-X) = kt$$

When the reaction is controlled by diffusion through product film (flat plate),

$$X^2 = kt$$

Where, 'X' is the degree of reduction, 'k' is the rate constant and 't' is the time.

3. Experimental Details

3.1 Materials

The ammonium paratungstate (APT) recovered from the tungsten-copper borings at NML was subjected to chemical analysis which was found to contain 99.95 % pure and the particle size was determined from particle size analyser and found to be in the range of 30 μm to 50 μm.

3.2 Experimental Set-up

The apparatus consists of a horizontal tubular furnace, argon and hydrogen gas cylinders with their regulators and rotameters, and alumina boat for reducing the sample. The schematic diagram was shown in Fig. 1. The hydrogen gas cylinder was connected through the rubber tube to the rotameters, which is further extended to a manifold before entering into the horizontal tubular reactor. The manifold was also connected to another rotameter and then to the argon gas through the regulator to pass the argon gas before and after the reduction experiment. The heating tube of the tubular furnace was made of inconel 600 with diameter of 6.5 cm and length 85.2 cm. The heating element of the tubular furnace was silicon carbide rods. The temperature was indicated and controlled using a Proportional Integral and Derivative (PID) controller with a Pt-Rh-Pt thermocouple. The even temperature heating zone of 10 cm of the tubular furnace was utilised for reducing the ammonium paratungstate. The both edges of the inconel tube were leak proof cover and also have the water circulating provision to cool the tube.
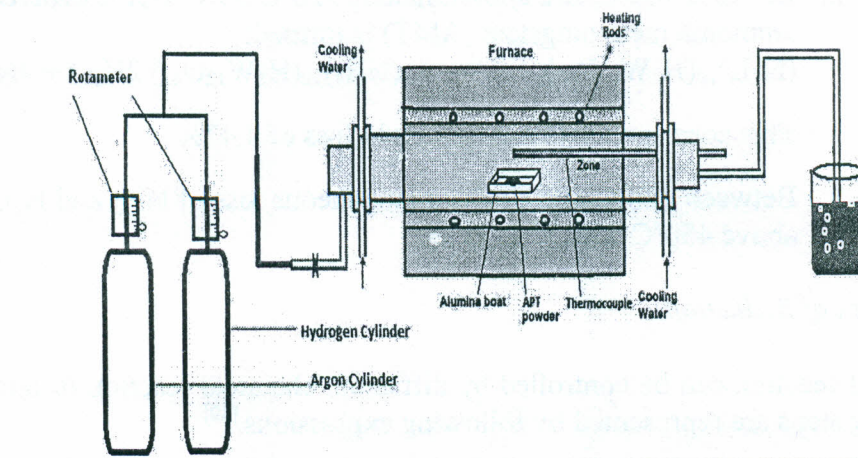

Fig. 1 : Schematic diagram of the experimental set-up

3.3 Procedure

During the process of reduction, the sample is loaded in alumina boat of length 9.3 cm width 4.0 cm, height 2.0 cm and thickness 2 mm which was then pushed into the furnace in the even temperature zone (10 cm of the furnace) using the iron rod and then the lid was closed. The predetermined hydrogen flow rate for the desired time interval and temperatures were controlled by the hydrogen rotameter. The hydrogen flow rate was used in between 0.1 to 0.3 lpm. Before starting the experiment and finishing the experiment the tubular furnace was flushed with argon gas, controlled by the argon rotameter. Thereafter the furnace was allowed to cool by the in-built facility of water cooling at both the edges of the inconel tube of the tubular furnace. The desired temperature of the furnace in the range 700 to 1000^0C for the various time intervals from 15 to 180 minutes was controlled by the Proportional Integral and Derivative (PID) controller. The flow of argon was stopped after the experiment was completed and the hydrogen flow was started. After completion of the experiment for the respective duration, argon flow was re-started for cooling down the boat with reduced sample to a temperature of around 400^0C. At room temperature, the boat was taken out and the decrease in weight due to reduction was calculated. All experiments were provided more than 2h time below the temperature of 650^0C in order to remove all the crystallised ammonia and water and subsequently the reducing temperature of 700 to 1000^0C was maintained for the desired time and flow rate. The reduced tungsten powder was sent for the X-ray diffraction (XRD) and electron probe micro analysis (EPMA) studies. The purity of tungsten powder was also determined by the chemical analysis. The kinetics was also evaluated for the respective temperatures.

4. Results and Discussion

4.1 Effect of Temperature

The influence of the various temperatures 700^0C, 800^0C, 900^0C, and 1000^0C at the time intervals of 15, 30, 45 and 60 minutes at 0.1 lpm hydrogen flow rate have been depicted in Fig. 2. The starting temperature of 700^0C was considered because till 450^0C[3] all the crystallised ammonia and water vapour goes out leading to a formation of blue tungsten oxide. The rate of reduction of tungsten oxide increases with the temperature at all time intervals. It is evident from the figure that for the temperatures from 700^0C to 900^0C with increase in time the percentage reduction increases. The rate of reduction increases with high rate with the increase in time up to 30 minutes, whereas in between 30 to 45 minutes there was moderate increase in the percentage reduction. At 700^0C, the percentage reduction increased from 2.78% at 15 minutes to 19.44% at 60 minutes. At 800^0C the percentage reduction increased from 8.33% at 15 minutes to 77.78% at 60 minutes. Similarly, at 900^0C the percentage reduction increased from 25% at 15 minutes to 99.9% at 60 minutes. Beyond 45 minutes, the increase of percentage reduction was higher and at 1000^0C, rapid increase in the reduction to 99.9% was observed. However, at a temperature of 800^0C going beyond 60 min upto 120 min, there was no further change in reduction value and was stable at 77.78%.

The XRD of the reduced sample and the synthetic tungsten powder is given in Fig. 3 and Fig. 4, respectively. Most of the observed d-values of actual tungsten powder were found to match with the d-values of synthetic tungsten powder (purity 99.99%) procured from market. The purity of the reduced tungsten powder was also determined by the chemical

analysis. It was found to contain more that 99.7% tungsten. The electron probe micro analysis with the microstructure was shown in Fig. 5. The size of the produced tungsten powder was found to be in the range of less than 10 μm (EPMA).

The H_2O/H_2 equilibrium ratio values obtained from the NASA report[4]. Thus the investigation of maximum values of (H_2O/H_2) at 1000^0C was in conformity with almost complete reduction of tungsten oxide at 1000^0C at 0.1 lpm in 60 minutes time.
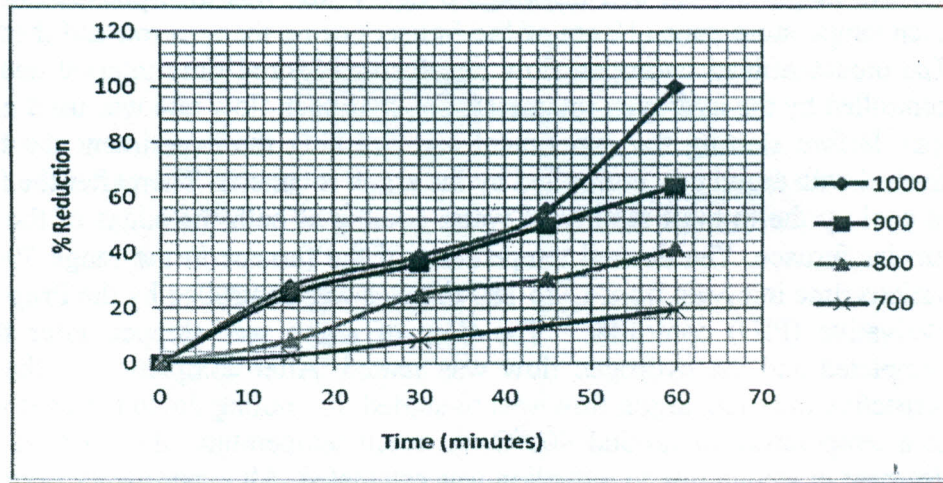
Fig. 2: Rate of reduction curves at different temperatures
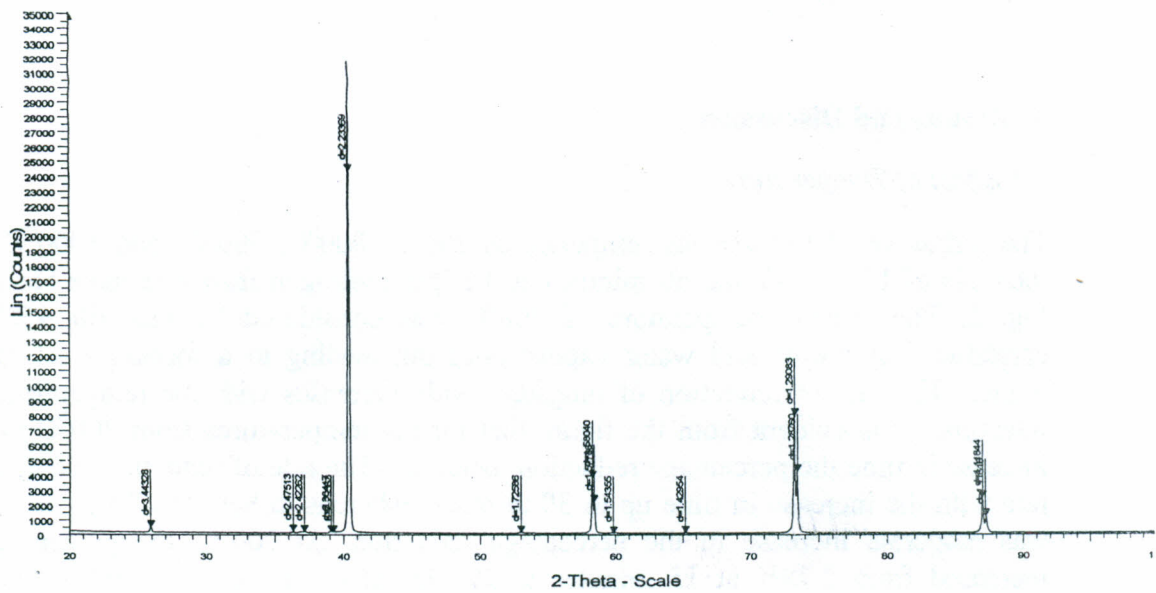
Fig. 3: X-ray diffraction pattern of the actual tungsten powder
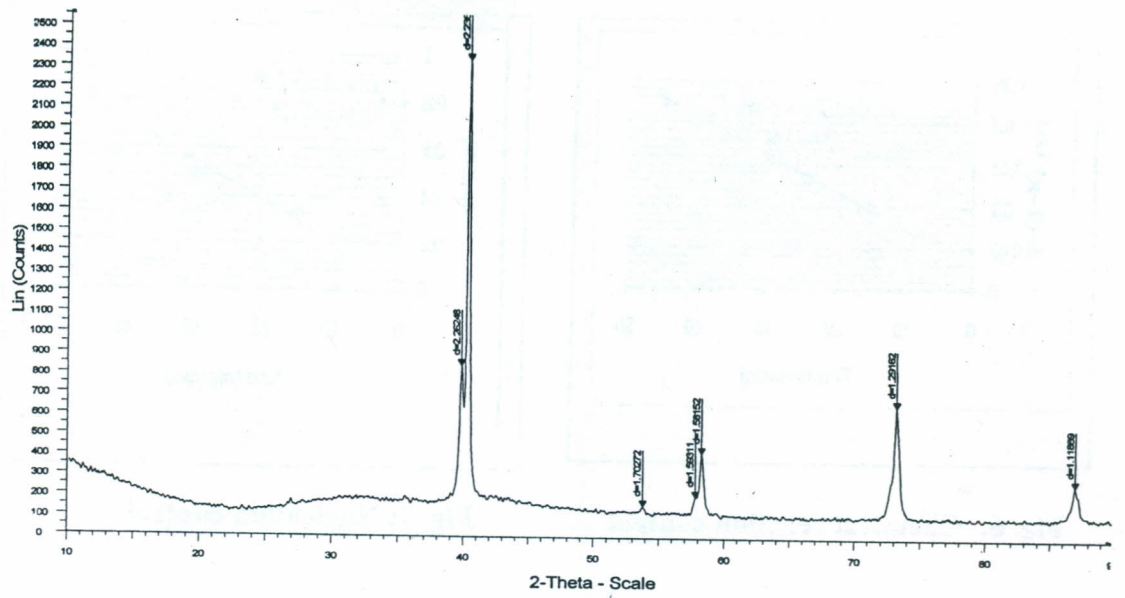
Fig. 4: X-ray diffraction pattern of the synthetic tungsten powder
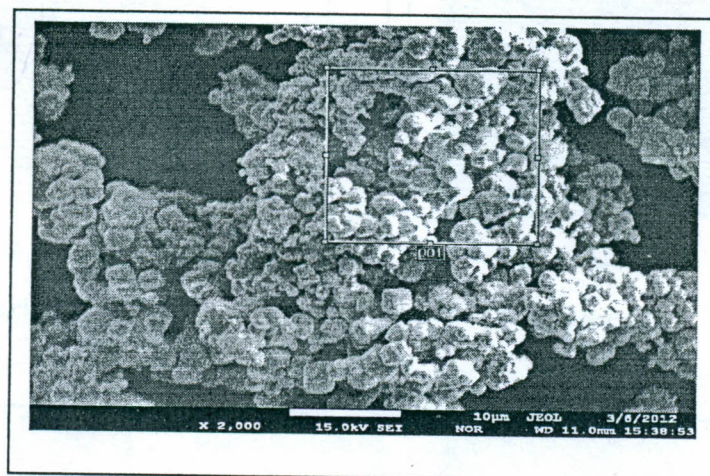
Fig. 5: Electron Probe Micro Analysis of tungsten powder

Evaluation of kinetic

The kinetics of tungsten reduction were evaluated at various conditions are given in Fig. 6 to Fig. 13. At all the reduction temperatures of 700^0C to 1000^0C the kinetics evaluated showed that chemical reaction rate control and nucleation control were the rates determining steps.
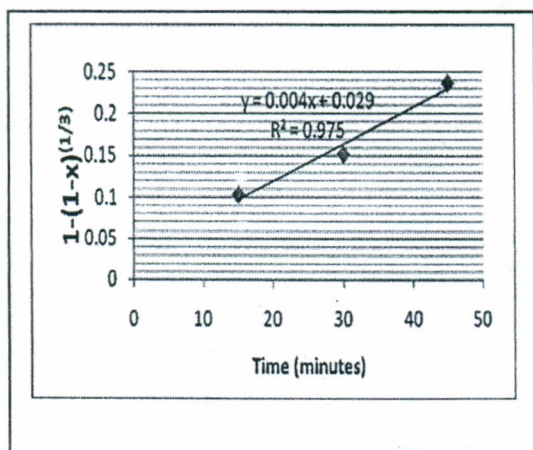
Kinetics of Reduction at 1000^0C and 0.1 lpm H_2 flow-rate:

Fig. 6: Chemical reaction control	Fig. 7: Nucleation control
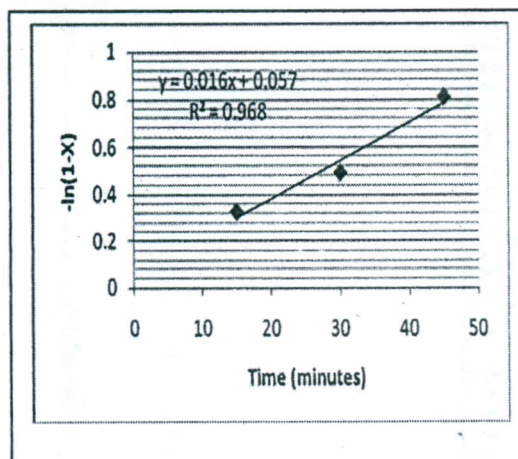
Kinetics of Reduction at 900^0C and 0.1 lpm H_2 flow-rate:
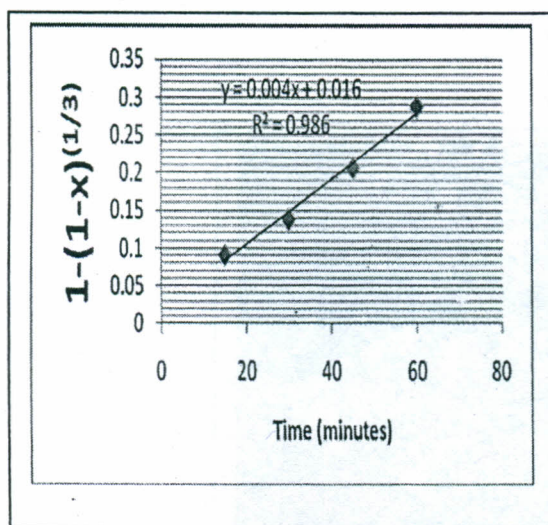

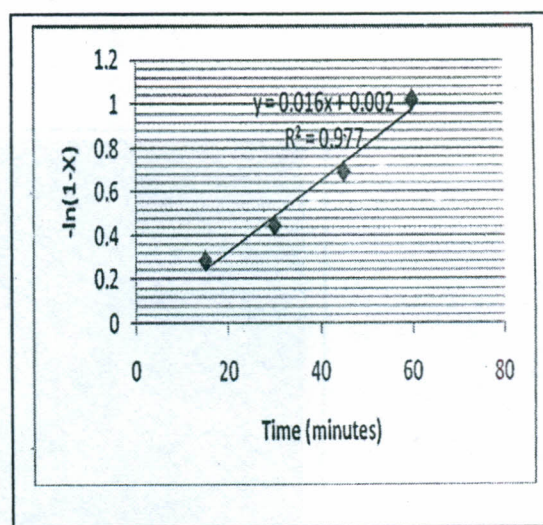|	
Fig. 8: Chemical reaction control	Fig. 9: Nucleation control

Kinetics of Reduction at 800^0C and 0.1 lpm (H_2 flow-rate)
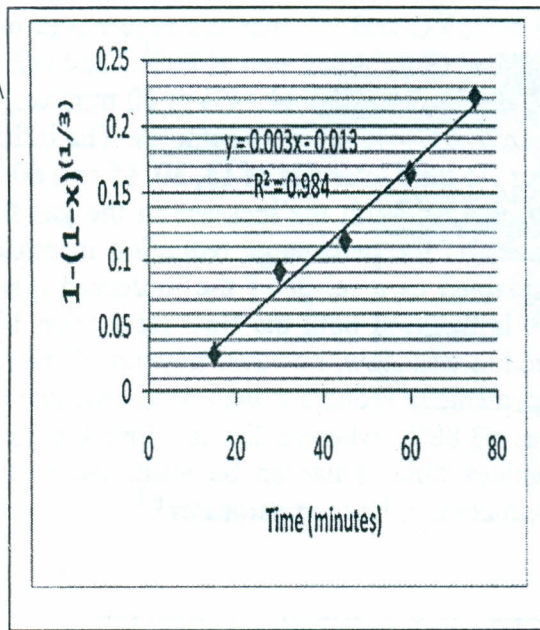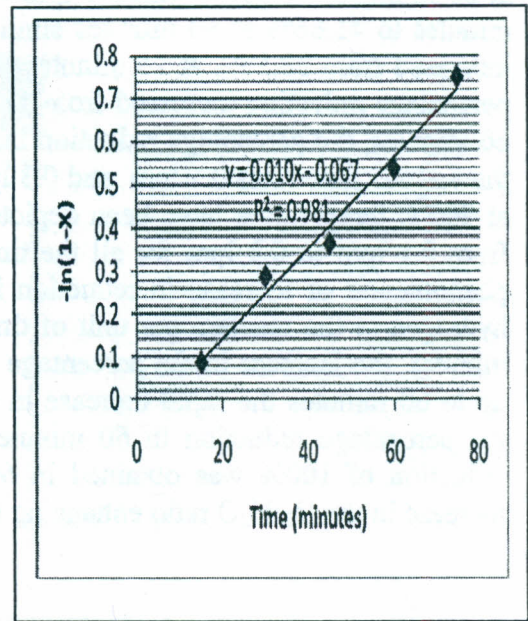

Fig. 10: Chemical reaction control

Fig. 11: Nucleation control

Kinetics of Reduction at 700^0C and 0.1 lpm H_2 flow-rate:
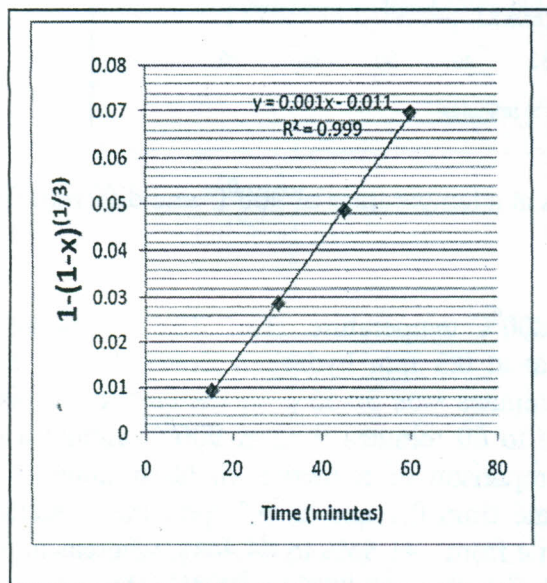

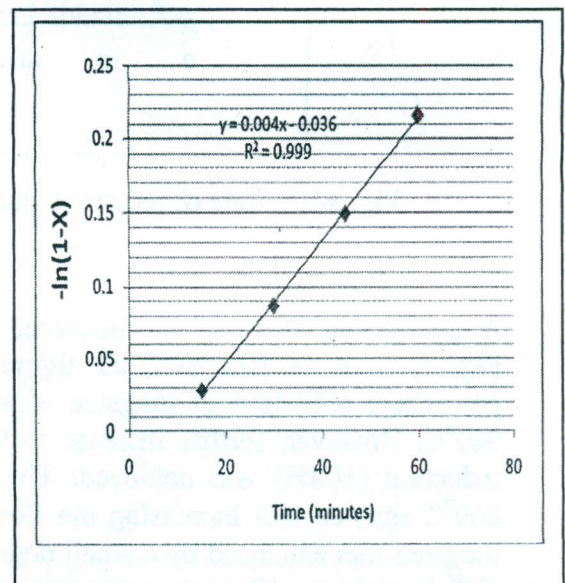**Fig. 12: Chemical reaction control**

Fig. 13: Nucleation control

4.2 Effect of Hydrogen Flow Rate

At 900^0C and 0.1 lpm the percentage reduction increased from 25% at 15 minutes to 63.88% at 60 minutes. At 800^0C and 0.1 lpm the percentage reduction increased from 8.33% at 15 minutes to 41.66% at 60 minutes similarly, at 900^0C and 0.3 lpm the percentage reduction increased from 30.55% at 15 minutes to 99.9% at 60 minutes also at 800^0C and 0.3 lpm the percentage reduction increased from 11.11% at 15 minutes to 44.44% at 60 minutes, beyond 60 minutes, the percentage reduction increased to 69.44% up to 75 minutes. The influence of the various flow rates 0.1 lpm and 0.3 lpm for the time intervals of 15, 30, 45 and 60 minutes at 900^0C temperature have been depicted in Fig. 14. With the increase in the gas flow rate from 0.1 lpm to 0.3 lpm for all the time intervals the percentage reduction increases. This phenomenon of increase in reduction is explained as a result of the increased quantity of hydrogen to the reactant per unit of time [5]. Initially, at both the flow rates from 15 to 30 minutes, the increase in the percentage reduction was slow, however beyond 30 minutes and up to 60 minutes the rapid increase in the percentage reduction was observed. For 0.1 lpm, the percentage reduction in 60 minutes was 63.88%, whereas for 0.3 lpm the percentage reduction of 100% was obtained in 60 minutes time. This can be attributed to the large increase in the H_2/H_2O ratio enhancing the reduction at low temperatures [6].
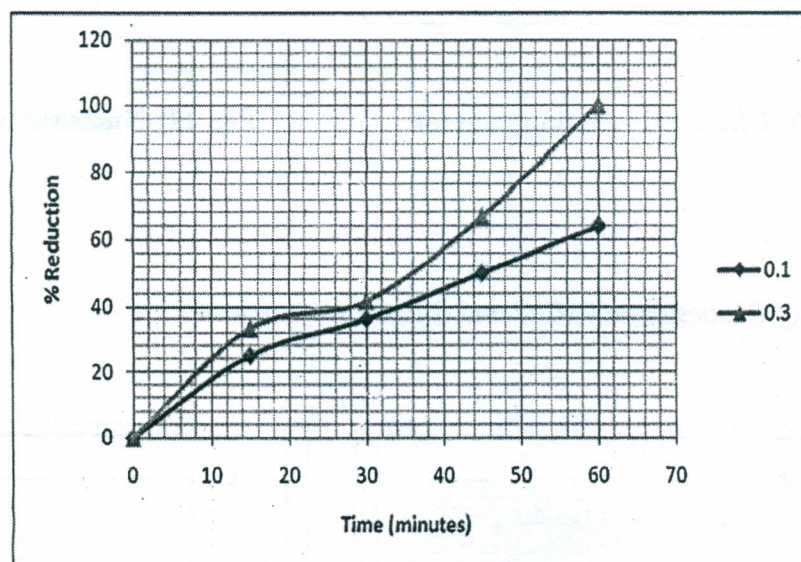

Fig. 14: Rate of reduction curves at a temperature of 900^0C and different flow rates

A similar kind of trend was observed at 800^0C temperature, also. The results are given in Fig. 15. It is evident from the figure that at 0.3 lpm hydrogen flow rate and 800^0C the percentage reduction of tungsten at 30 minutes was 30.55% in comparison to 44.44% at 900^0C. However, further increase in time to 60 minutes time at 900^0C almost a complete reduction (100%) was achieved. The comparison of reduction in 60 minutes duration at 800^0C showed that increasing the flow rate from 0.1 lpm to 0.3 lpm, the reduction of the tungsten was enhanced by a small degree i.e from 41.66% to 44.44%, whereas at 900^0C the difference in the 60 minutes time was high (i.e from 63.88% to 100%). On comparison with the complete reduction of APT at 1000^0C, 0.1 lpm hydrogen flow rate in 1h time with that of reduction of APT at 900^0C, 0.3 lpm hydrogen gas flow rate in 1h time it can be inferred that

decreasing the temperature by 100^0C the amount of hydrogen gas required was increased by 3 times.
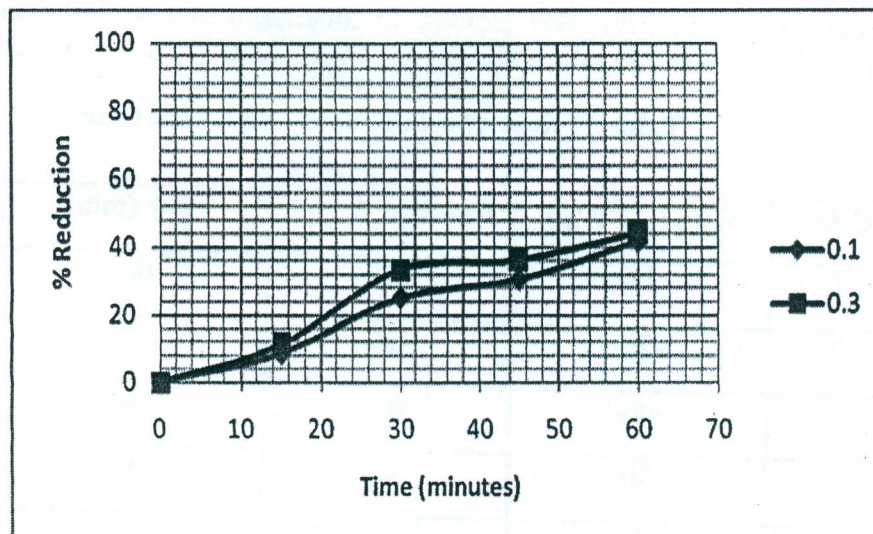

Fig. 15: Effect of flow rate at 800^0C

4.3 Effect of Time

At 800^0C and 0.1 lpm, given in Fig. 16, the rate of reduction increased from 8.33% at 15 minutes to 25% at 30 minutes, with further increase in time from 30 minutes the rate of reduction increased to 30.55% at 45 minutes and then to 52.77% at 75 minutes. Beyond which the rate of reduction became constant at 77.78% at 90 minutes and the further increase in time to 120 minutes was unable to enhance the extent of reduction.
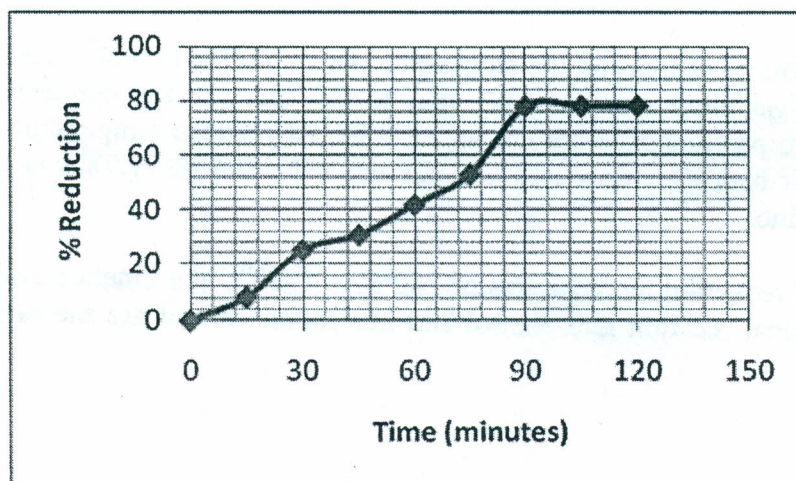

Fig. 16: Rate of change of reduction with time at 800^0C and 0.1 lpm flow rate of hydrogen gas

4.4 Reduction of ammonium paratungstate at higher scale

The results of the experiments carried out at 10 gm scale (1.3 mm bed-depth) are given in Table 1. At this scale with temperature of 1000^0C and 0.1 lpm in 60 minutes time the rate of

reduction decreased more than 50% and was found to be 46.40%. The further increase in time from 60 to 120 minutes the rate of reduction increased to 86.97%. Further increase in time to 180 minute almost complete reduction was observed.

Experiments carried out at 30 g scale and bed-depth of 4 mm exhibited the increase in reduction from 79.51% 90.97% with increase in time from 180 to 240 minutes. Further increase in time for another 120 minutes could not enhance the reduction percentage.

Table 1: Rate of reduction of APT with time

S.No	Wt. of APT (g)	Bed-depth (mm)	Time (min)	Reduction %
1	10	1.3	60	46.40
2	-do-	-do-	120	86.79
3	-do-	-do-	180	99.99
4	30	4	180	79.51
5	-do-	-do-	240	90.97
6	-do-	-do-	300	90.97

5. Conclusions

(i) The complete reduction of ammonium paratungstate is obtained at the optimised conditions of 1000^0C, 60 minute time, and 0.1 lpm flow rate of hydrogen gas at 2g scale.

(ii) The benefits of decreasing the temperature from 1000^0C to 900^0C and increasing the hydrogen gas flow rate from 0.1 lpm to 0.3 lpm for the complete reduction of ammonium paratungstate are not appreciable. At reduced temperature of 800^0C and 0.1 lpm of hydrogen flow rate a maximum reduction of 77.78% is obtained in 90 minutes time.

(iii) At all the reduction temperatures of 700^0C to 1000^0C the kinetics evaluated showed that chemical reaction rate control and nucleation control are the rates determining steps.

REFERENCES

1. S. N. Bhosale, S. Mookherjee and R.M. Pardeshi 1990, *High Temperature Materials and Processes*, Vol. 9, pp. 2-4.

2. Fathi Habashi, *Handbook of Extractive Metallurgy.* Vol-III, 1997 and Publication Wiley-VCH,

   D69451 Weinheim, Federal Republic of Germany, pp. 1330-1359.

3. M. H. Ghandehari, J. K. Faulkner, and M. J. Schussler, Electrochem. Soc.: *Electrochemical Science and Technology,* 1982, 129(12), pp. 2666-2668.

    India, 2007, pp.67-71.

4. V. D. Barth and H. O. Mcintire, Tungsten powder metallurgy, *Technology Utilization Report, NASA SP-5035*, November 1965.

5. W U Xiang-Wei, LU Bi-Zhi, XIE Chen-Hui, PI Shy-Ming, YI Dan-Qing, Crystal growth of tungsten during hydrogen reduction of tungsten oxide at high temperature, *Transaction of Nonferrous Metals Society of China*, 15 September 2009, s785-s789.

6. Dean S. Venables, Michael E. Brown, Reduction of tungsten oxides with hydrogen and with carbon, *Thermochimica Acta 285, 1996*, pp.361-382.