Reduction of tungsten trioxide with ethanol

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A B S T R A C T

This study aims to investigate pyrometallurgical reduction behavior of tungsten trioxide by ethanol at the temperature range 900–1500 K. Thermodynamic analysis predicted single tungsten phase formation from tungsten trioxide and ethanol at the temperature range studied. The experiments were carried out in a flowing ethanol (7.1 vol.%)-Ar atmosphere in a tube furnace for various reaction periods of time. The extent of the reduction was followed by mass measurements. XRD and SEM were used to carry out phase and morphological studies on the products obtained at various stages of the reduction. It was found that at the temperature range 900–1200 K, oxide reduction was incomplete owing to sluggish reaction kinetics between the reactants. At higher temperatures of 1300 K, 1400 K, and 1500 K, tungsten trioxide reduction to metallic tungsten was complete within ~45 min, ~30 min and ~20 min, respectively. Well-facetted tungsten particles with mean sizes of 1.6 μm, 2.1 μm and 3.3 μm were observed at these conditions. At 1500 K, there was a significant tungsten loss by the flowing gas stream via the formation of gaseous $WO_2(OH)_2$. Possible reaction pathways leading to metallic tungsten were discussed.

1. Introduction

Because tungsten offers superior properties such as high density, high melting point, high modulus of elasticity, low thermal expansion, low vapor pressure and good corrosion resistance, it is used as a major constituent for various parts such as radiation shields, heating elements, kinetic energy penetrators, and balance weights. Furthermore, it is also employed in the production of tungsten carbide for wear resistant parts (such as cutting tools, dies, nozzles).

Tungsten is conventionally produced from tungsten oxide. Primary sources for tungsten oxide are wolframite ((Fe,Mn)WO_4) and scheelite (CaWO_4) ores. Tungsten-containing scrap materials are also used as secondary sources which are converted to tungsten oxide (for example, WO_3) by hydro/pyrometallurgical processes. Tungsten oxide is then reduced to metallic tungsten usually by hydrogen. Hydrogen is widely used for the reduction of metal oxides. But, it is relatively expensive. Tungsten oxide is also reduced by carbothermic reactions using solid carbon (graphite, carbon black). But, carbon is always a source of increased tungsten contamination because it contains impurities like Ca, Si, Fe, S, and P [1]. Recently, methane (CH_4) has been used as an alternative reducing agent to obtain metallic W from WO_3 because it is relatively cheap and abundant (a main component of natural gas) [2].

In the present work, we have chosen liquid ethanol (C_2H_5OH) as a reducing agent source because it is high in hydrogen content, renewable, increasingly available, easy to transport, safe to handle,

biodegradable, low in toxicity and produced in large quantities from various sources such as biomass, plants, wasted materials. To the best of our knowledge, no report has been published on reduction of tungsten trioxide with ethanol. The present study aims to investigate pyrometallurgical reduction behavior of WO_3 in a flowing atmosphere containing C_2H_5OH. Furthermore, thermodynamic analysis in the WO_3-C_2H_5OH-Ar system was carried out in order to predict and understand reaction pathways leading to the formation of metallic W.

2. Thermodynamic analysis

The analysis was done by a method of minimization of the Gibbs' free energy of a system [3]. For a system of known input composition, it computes both the equilibrium gas phase and condensed phase compositions at a given pressure and temperature. The calculation requires specifying all possible species and condensed phases known to exist in the temperature range of interest. In the present study, WO_3 and C_2H_5OH were used as reactants and Ar was used to carry C_2H_5OH vapor into the furnace. Hence, the equilibrium calculations were carried out in the W-O-C-H-Ar system at the temperature range 1200–1500 K at a pressure of 1 atm for an Ar/C_2H_5OH molar ratio of 13.1, which is experimentally attainable. In this system, 47 species were considered to be as the constituents of the gas phase. They include H_2, CH_3, CH_4, C_2H_4, C_3H_6, C_4H_6, C_6H_6, C_7H_8, C_2H_2O, H, OH, H_2O, $WO_2(OH)_2$, W_2O_6, W_3O_8, W_3O_9, W_4O_{12}, CO and CO_2. Condensed equilibrium phases were assumed to be WO_3, WO_2, W, W_2C, WC and C. Solid tungsten oxide compounds with lower oxygen contents (WO_{3-x}) were excluded from the calculations for the sake of clarity. Input thermodynamic data in the

form of Gibbs' free energy of the formation of the constituents were obtained from the thermochemical tables [4,5].

Fig. 1 shows the solid phase fields computed as a function of temperature and input C_2H_5OH mole fraction (X_{C2H5OH}) which is given by $n^o_{C2H5OH}/(n^o_{C2H5OH} + n^o_{WO3})$ where n^o represents the input numbers of moles of the reactants. The boundaries in the diagram divide different phase fields in which the indicated phases are expected to form from C_2H_5OH and WO_3. As can be seen from the figure, $WO_3 + WO_2$, WO_2, $WO_2 + W$, W, $W + WC$, WC and $WC + C$ fields appear successively as the ethanol content (X_{C2H5OH}) is increased. Single W phase field widens as the temperature is increased. For example, the X_{C2H5OH} ranges in which single W phase forms are predicted to be 0.524–0.685 at 1200 K and 0.471–0.750 at 1500 K. The analysis indicates that WO_3 can be reduced to W by C_2H_5OH and confirm that the reduction follows the path of $WO_3 \rightarrow WO_2 \rightarrow W$. The intermediate and overall dominant reactions in connection with this path will be elucidated later in Section 4.4.

3. Experimental procedures

The experimental set-up used for the present study essentially consists of a hot-wall furnace with SiC heating elements, a bubbler for ethanol, an alumina tube (20 mm in diameter and 500 mm in length) and Ar gas flow meter. The chemicals used for the present study were Ar, C_2H_5OH and WO_3 powder (≥99.5%). XRD and SEM revealed that the oxide powder is stoichiometric WO_3 and consists of nearly round particles with a mean size of 28 ± 7 nm [2].

An alumina boat was used as a powder holder and its gas entrance side was cut to allow smooth gas flow. It was loaded with ~250 mg WO_3. Moisture in the powder was removed at 373 K in an oven prior to the experiments. The oxide powder was heated at a rate of ~35 K/min in a flowing Ar atmosphere (85 standard cm^3/min, sccm) to the reaction temperatures for all the experiments. When the desired temperature was reached, Ar flow was directed into the liquid ethanol bath kept in a bubbler at 296.5 ± 1 K to carry the vapor into the furnace. The flow rate of gaseous ethanol ($F^o_{ethanol}$) carried by Ar (85 sccm) was calculated to be 6.5 ± 0.4 sccm by the following formula:

$$F^o_{ethanol} = \frac{F^o_{argon} P_{ethanol}}{P_{total} - P_{ethanol}} \qquad (1)$$

where F^o_{argon}, $P_{ethanol}$, and P_{total} are flow rate of the carrier gas Ar, ethanol vapor pressure (0.0708 atm) at 296.5 K and total pressure (1 atm), respectively. All the experiments were done at a constant Ar/C_2H_5OH molar ratio of 13.1 (7.1 vol.% ethanol). The experiments were carried out at the temperature r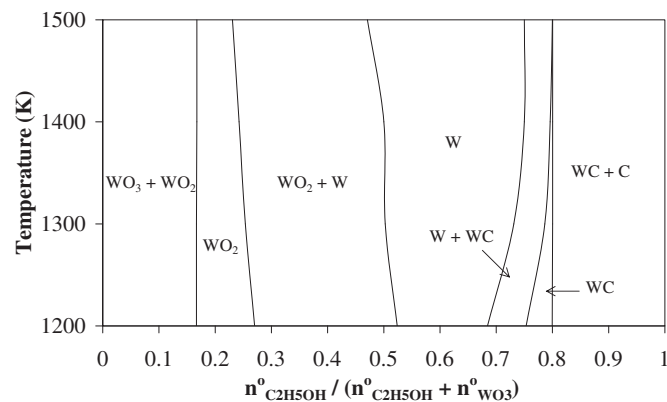ange 900–1500 K for various isothermal holding periods of time. After the reaction, all the products were cooled rapidly to the room temperature in a flowing Ar atmosphere.

Mass measurements before and after the experiments were carried out at room temperature by a calibrated electronic balance (Sartorius BP110S) with a sensitivity of ± 10^{-4} g in order to determine the extent of the reaction. Change-in-mass was calculated using the equation of $(m - m_o)/m_o \times 100$ where m is the mass at temperature T and time t and m_o is the starting mass of the oxide.

Morphological analysis of the products was carried out by a Field-Emission Gun Scanning Electron Microscope (Zeiss Supra 55 VP). Mean particle sizes were determined from the areas of at least 50 particles using SEM images. Equivalent circular diameters of the measured areas were calculated to describe mean particle sizes. Phases in the samples were determined by a parafocusing X-ray diffractometer (RIGAKU D/Max-2200 XRD) equipped with a Cu radiation tube ($\lambda_{K\alpha}$ = 0.15418 nm) and a monochrometer at a scanning rate of 2°/min.

4. Results and discussion

4.1. Effects of temperature and time

The percentage mass changed as a function of time at the temperatures investigated is shown in Fig. 2. Horizontal dashed line in the figure represents the theoretical mass loss (20.70%) calculated for the full reduction of WO_3 to W. This line may be taken as a reference for full oxide reduction. It was noted that the mass changes for 0 min were −1.47%, −0.92%, −0.56% at 1500 K, 1400 K and 1300 K, respectively, indicating that WO_3 losses small amount of oxygen during heating in pure Ar atmosphere. The mass loss increases to a certain extent with reaction time and temperature as can be seen from the figure. At the temperature range 900–1200 K, the mass loss was slow and well below the mass loss expected for the complete reaction. For example, at 1200 K, the mass loss is 8.15% for 60 min. Full reduction of WO_3 to W is not practically possible at the temperature range 900–1200 K under the experimental conditions studied. At and above temperature 1300 K, however, higher mass loss values are observed as seen from Fig. 2. At 1300 K, the mass loss increases initially with time from 15.51% at 30 min to 22.35% at 45 min at which a minimum appears. The mass loss at 45 min is found to be slightly less than the theoretical one, suggesting that the oxide reduction is complete. As the reaction time is increased to 60 min, there is a slight mass gain which is attributable to C uptake by the powder. At higher temperatures (1400 K and 1500 K), the reaction behavior of the oxide is observed to be similar to that at 1300 K. But, the minima are observed in shorter reaction periods with increasing temperature.
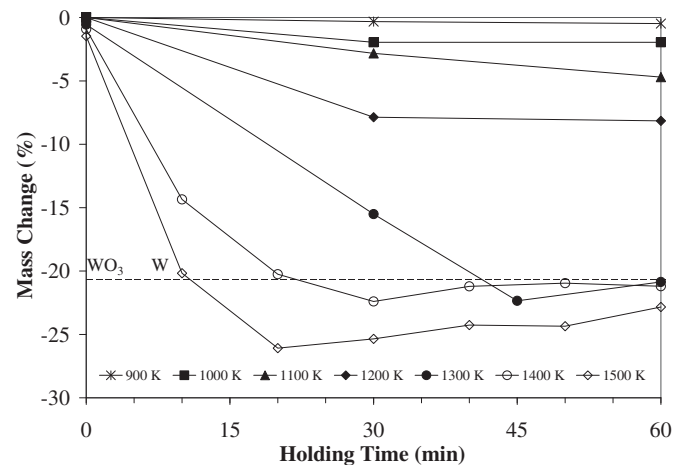

Fig. 1. Equilibrium diagram showing solid phase fields as a function of temperature and input C_2H_5OH mole fraction (X_{C2H5OH}) in the WO_3-C_2H_5OH-Ar system. Ar/C_2H_5OH molar ratio is kept constant at 13.1.

Fig. 2. Influence of reaction temperature and isothermal holding time on the mass change in WO_3 powder in Ar-C_2H_5OH atmosphere. Horizontal dashed line represents the theoretical mass change for the full reduction of WO_3 to W.