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Preparation and characterization of tungsten powder through molten salt electrolysis in a $CaWO_4$–$CaCl_2$–NaCl system

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ABSTRACT

In the present study, preparation of tungsten powder from a $CaWO_4$–$CaCl_2$–NaCl system using a molten salt electrolysis method was investigated. Analytical techniques, such as scanning electron microscopy equipped with EDS and XRD, were respectively used to study the microstructure and phase evolution of the resulting powder. AES and the Fisher method were used to analyze the purity and particle size of the samples, respectively. The current efficiency during electrolysis was studied based on the experimental data. Thermodynamic properties of electrolysis process were studied using cyclic voltammetry. The results showed that tungsten powder could be prepared at a temperature of 750 °C and a cell voltage of 2.5 V for 250 min. The electrode reactions occurring in the stable electrolysis region were irreversible, and kinetic obstruction of electrolysis could be derived from the low solubility of calcium tungstate in the $CaCl_2$–NaCl melt.

1. Introduction

Tungsten is used in many fields, and its consumption has increased yearly because of its excellent physical and chemical properties, which include high melting point, low vapor pressure, high hardness, and exceptional acid resistance. The existing metallurgical processes of preparing tungsten powder are complex, expensive, and likely polluting [1,2]. Molten salt electrolysis is well known for its effectiveness in producing refractory metals [3,4]. Therefore, application of the molten salt electrolysis method for the direct preparation of tungsten metal powder from solid tungstate is highly desirable for developing simple, low-cost, and environmentally sound processes to meet increasing demands for tungsten metal. During the 1960s and 1970s, tungsten powder was reported to be prepared through molten salt electrolysis [5,6]. During the 1990s, Feng and coworkers [7,8] studied the electrochemical formation of tungsten powder via molten salt electrolysis in KCl–NaCl–Na_2WO_4–WO_3, and NaCl–Na_2WO_4–WO_3 systems. Erdoğan and Karakaya [9] recently focused on the direct electrochemical production of tungsten via an electrolysis setup, which is, in some ways, similar to the FFC Cambridge process.

With this background, a method for the direct preparation of tungsten powder via electrochemical reduction of $CaWO_4$ from $CaCl_2$–NaCl melts was proposed. In this process, inexpensive and easily stored $CaWO_4$, which has a low melting point, and weak and corrosive $CaCl_2$–NaCl melts are used as raw materials to determine whether or not they are beneficial for industrial tungsten production [10,11].

2. Experimental

2.1. Raw materials and methods

The raw materials used in the experiments were $CaCl_2$, NaCl, and $CaWO_4$ (99.5% purity; China). Mixtures of $CaCl_2$–NaCl ($CaCl_2$: NaCl = 1:1 mol.%, 475 g) with $CaWO_4$ (25 g) were used to fill a corundum crucible and dehydrated at 300 °C for 24 h to 36 h. The electrolytic cell voltage and temperature were 2.5 V and 750 °C, respectively. A graphite rod (d = 8 mm) served as the cathode, and a graphite rod (d = 12 mm) served as the anode. The electrolysis time was 250 min.

After electrolysis, samples of the electrolytic products obtained at the bottom of the corundum crucible were immersed in 1.5 N HCl for approximately 10 h. Thereafter, the samples were rinsed with distilled water and dried in air at 120 °C. The end-product particles were characterized by X-ray diffraction (Miniflex, Japan), scanning electron microscopy (XL30W, The Netherlands), and energy dispersive spectroscopy (EDAX, USA). Atomic emission spectroscopy (Shimadzu, Japan) was used to analyze the purity of the end-products. The particle size of sample powders was analyzed using the Fisher method. Samples obtained from a cathodic surface layer were analyzed by X-ray diffraction (Miniflex, Japan). A Gastec portable gas detection pipe (H-7001, China; GASTEC, Japan) was used to detect CO_2 and CO concentrations in the exhaust gas. Electrochemical analysis was carried out using an electrochemical workstation (Auto lab, PGSTAT301, The Netherlands).

2.2. Experimental apparatus

The electrochemical reduction units are shown in Fig. 1. A gas-tight electrolytic cell was made so that electrolysis could be performed in an

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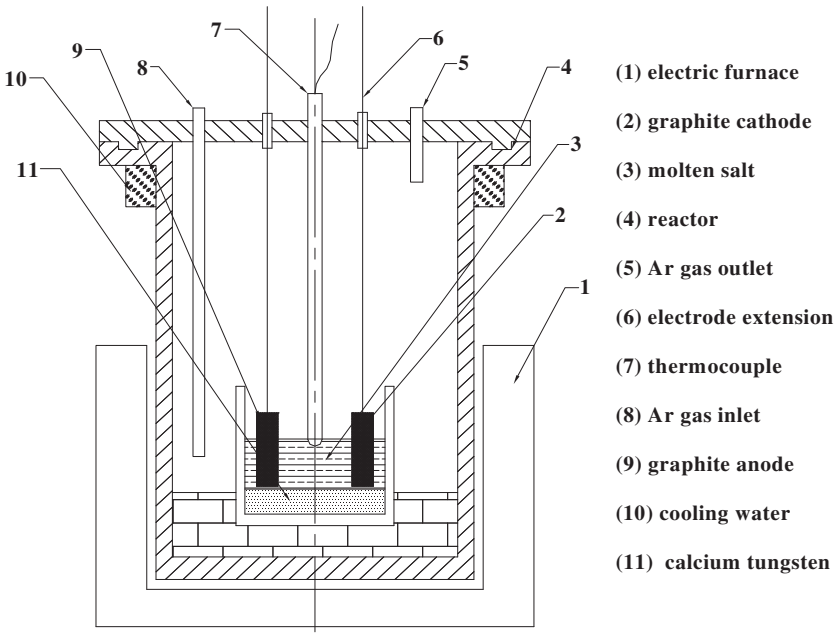

Fig. 1. Schematic drawing of the experimental apparatus.

inert atmosphere of dry, high-purity argon. All electrical connections from the individual electrodes to the power supplies were made using copper wires. The electrolyte temperature was measured using a type-K thermocouple in alumina crucibles.

3. Results and discussion

3.1. Characterization of samples

After electrolysis, cathodic surface layers (0.2 mm to 0.5 mm) were scraped and analyzed by XRD; typical XRD patterns are shown in Fig. 2. The patterns of the powders obtained from the cathodic surface layers show that the sample was composed of W, W_2C, WC, and a small amount of C. Based on literature data [12], formation of WC and W_2C as a result of the reaction between the produced W and C cathodes is spontaneous at 750 °C in thermodynamic conditions, but the reaction only occurs on the surface layer of the cathode. When the electrolytic run is sustained, the tungsten power synthesized around the cathode is deposited to the bottom of the electrolytic cell because of its high density.

A typical XRD pattern of the end-products is shown in Fig. 3. All the characteristic peaks of tungsten are present in the electrolyzed sample. The results conclusively prove that $CaWO_4$ is reducible to tungsten in the molten $CaCl_2$–NaCl eutectic. SEM and EDS allow further analysis and characterization of the electrolyzed sample. SEM images of the end-products are presented in Fig. 4, and EDS analysis of parts A and B in Fig. 4 is given in Table 1. The particle size of the tungsten powders was observed to be less than 5 μm, and the crystallized particles presented as individual, continuous, and bunchy grains. EDS results show that the electrolyzed sample was essentially composed of tungsten metal with low levels of oxygen. The presence of oxygen in the electrolyzed sample is proof of incomplete reduction. However, from the data presented in Table 1, over 95% of the electrolyzed sample mass was calculated to be tungsten metal, assuming that the impurity was WO_3.

As EDS only gives information about the surface structure of the products, the purity of tungsten was analyzed using an emission spectrographic method to support the computations given. The results of main impurity elements and trace impurity elements in the samples are shown in Tables 2 and 3, respectively.

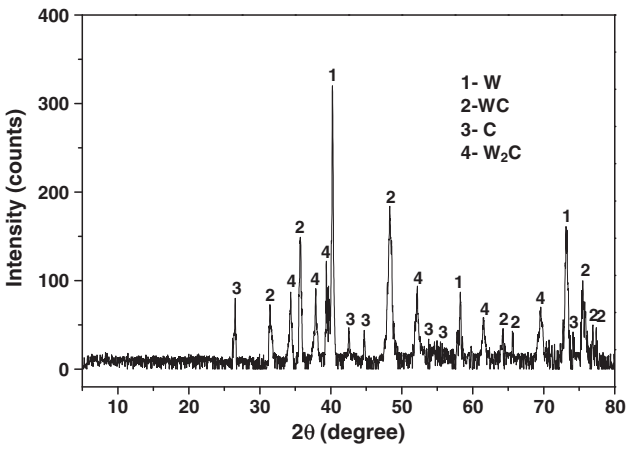

Fig. 2. XRD patterns of samples on cathodic surface layer.

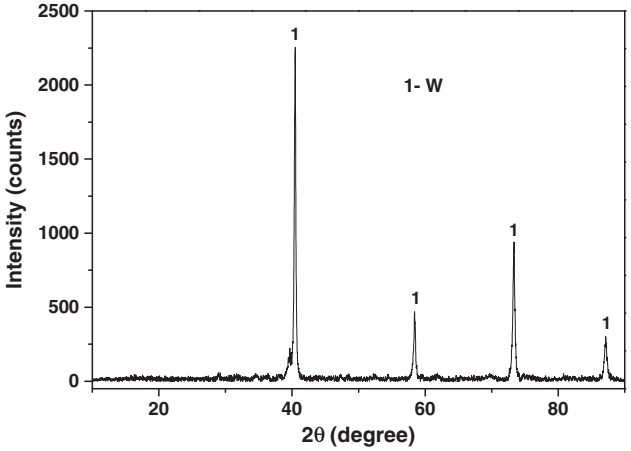

Fig. 3. XRD patterns of samples for 250 min electrolysis.