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Decomposition-carbonization of ammonium paratungstate in a fluidized bed

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ABSTRACT

In this study, the reduction-carbonization property of WO_3 obtained by thermal decomposition of ammonium paratungstate (APT) under N_2 and air atmosphere in a fluidized bed was investigated. The decomposition property of APT in N_2 and air was analyzed by TG analyzer. Phase, morphology, deoxidation rate and carbonization rate of the decomposed products in the reduction-carbonization process were investigated. It was found that APT could be rapidly decomposed into monoclinic WO_3 in a fluidized bed in N_2 or air atmosphere. Compared with N_2 atmosphere, air was more favorable for the rapid decomposition of APT and the crystal transition of WO_3. Under the same conditions, the products obtained in N_2 atmosphere had smaller grain size, larger porosity, faster deoxidation rate and carbonization rate. Both WO_3 obtained in the N_2 and air could be reduced and carbonized to nano-sized WC with S_{BET} particle sizes of 63.70 nm and 73.49 nm in a fluidized bed, respectively.

1. Introduction

Ammonium paratungstate $(NH_4)_{10}[H_2W_{12}O_{42}]\cdot 4H_2O$ (APT) is the main tungsten compound used in the manufacturing of tungsten products, such as tungsten oxides, metallic W, WC powder and alloy products [1]. In industry, tungsten/WC is produced from its oxide (WO_3/$WO_{2.72}$) through the decomposition of ammonium paratungstate (APT). The preparation and subsequent thermal decomposition of APT to produce high-purity WO_3 is a fairly well-known process, widely used in the tungsten industry. Obviously, the first step, namely decomposition is very important for the preparation of ultrafine or nano-sized tungsten/WC. Research indicated that particle size and morphology of tungsten/WC powder were considerably influenced by the size and morphology of the oxides, which, in turn, depended on the characteristic features of APT [2,3].

Therefore, numerous researchers have studied the decomposition performance of APT, including the kinetics and mechanism [4,5], the change of structures and morphologies during the decomposition process [6,7]. Results indicated that WO_3 with different crystalline forms could be obtained as APT decomposed at different conditions [8]. For instance, ammonium tungsten bronze (h-ATOB), $(NH_4)_{0.33}WO_3$, and WO_3 with hexagonal type were identified in the calcination of APT at 400 °C for 2 h under static air. On heating up to 497 °C, ammonium tungsten bronze together with hexagonal WO_3 transformed completely into triclinic tungsten trioxide. Madarász et al. [9] studied the thermal decomposition of APT in air atmosphere, they found that monoclinic WO_3 (m-WO_3) was formed together with hexagonal h-ATOB when the temperature rose to 500 °C. Thus, WO_3 with different crystal forms and morphologies will be obtained under different conditions.

To obtain ultrafine tungsten or nano-sized WC, nano-needle violet tungsten oxide has attracted people's attention, which is produced by the reduction of H_2 generated from the ammonia decomposition in a closed rotary furnace [2]. Therefore, at present, in the ultrafine tungsten powder or tungsten carbide production, APT decomposition is mainly carried out in a rotary furnace. However, ring-forming easily to happen for that the water vapor cannot be ruled out rapidly. Comparatively speaking, the fluidized-bed decomposition of APT offers a number of distinct advantages such as lower decomposition temperature as well as time, faster kinetics, and better product morphology. Tripathy et al. [10] concluded that the temperature and holding time for achieving complete decomposition in a batch reactor were found to be much higher as compared to the respective values obtained in a fluidized-bed reactor using air as the fluidizing medium.

Although the decomposition characteristics of APT have been extensively reported, the reduction-carbonization properties of decomposed products under different conditions (such as temperature, atmosphere) have not been reported, especially by fluidization technology. Moreover, there are still some questions need to be answered. For example, the relationship between the different crystal types and surface morphologies of the decomposed samples and the reduction-carbonization rate, and the grain size of tungsten or tungsten carbide, etc.

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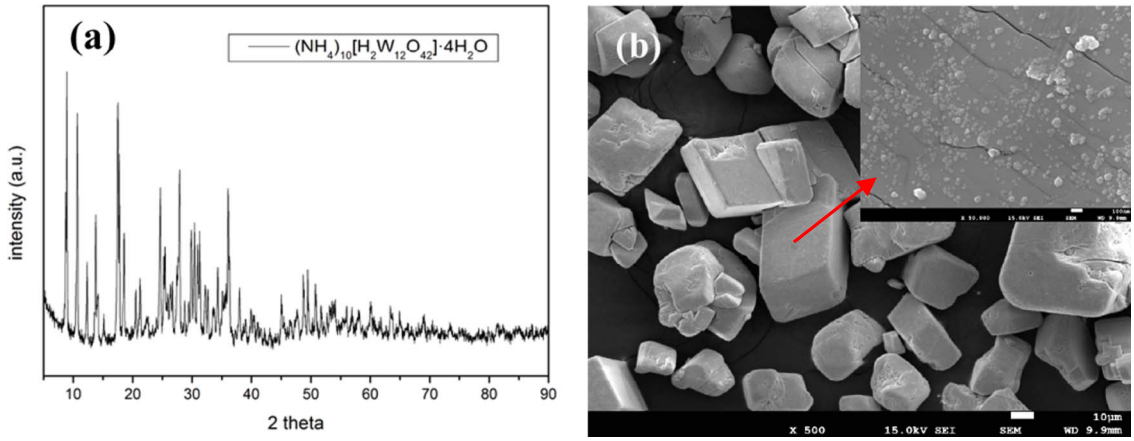

Fig. 1. (a) XRD pattern and (b) SEM image of the raw APT powder.

Therefore, the aim of this paper is to investigate the reduction-carbonization performance of the decomposed samples under N_2 and air conditions in a fluidized bed.

2. Experimental

2.1. Materials

Commercial ammonium paratungstate (APT) was obtained from Ganzhou Huamao Tungsten Materials Co. Ltd. The phase and micrograph of the powders were shown in Fig. 1. XRD pattern was in good agreement with the XRD pattern of APT4 given in the cards of ICDD 040-1470 where the chemical formula is given as $(NH_4)_{10}(H_2W_{12}O_{42})\cdot 4H_2O$ and the crystal structure as monoclinic. The shapes of the particles were angular, sub angular and with dense surface (as could be seen in the inserted figure), some cracks could be found in some particles. Compressed air and high purity (99.99%) CO and N_2 were used as experimental gases.

2.2. Experimental procedures

Fig. 2 represented the schematic diagram of the experimental setup. A 20 mm diameter (internal) and 700 mm long quartz tube, vertically placed, was used for carrying out the decomposition and reduction-carbonization studies. The middle of the reactor was fitted with a quartz distributor (0.04 mm pore) for the upward movement of air/N_2 and reducing gas from the compressor. The flow meters and valves were used to control the gas velocity. The reactor was heated externally by resistance wires, wound on the reactor tube, from outside. For decomposition experiments, APT powder was added into the reactor as the temperature reached the setting value under air/N_2 atmosphere. For carbonization experiments, to avoid the change of crystal structure and size of the decomposed products at high temperature, the decomposed powder was directly poured into the fluidized bed CO atmosphere when the reactor reached the desired temperature as measured by the inserted thermocouple. After the desired time of reaction, the reactor was removed from the hot zone of the furnace and quenched directly by spraying water on its outer surface, and then the as-reduced samples were collected and subjected to various characterizations.

2.3. Analysis and characterization

Phase analysis was detected on PANalytical X'pert diffractometer with Cu Ka radiation (k = 1.5408 Å). Thermal analysis of APT was carried out in TGA-DTA equipment (TG-DTA6300). During the thermal analysis, the sample was placed in corundum crucible. Dry air and high

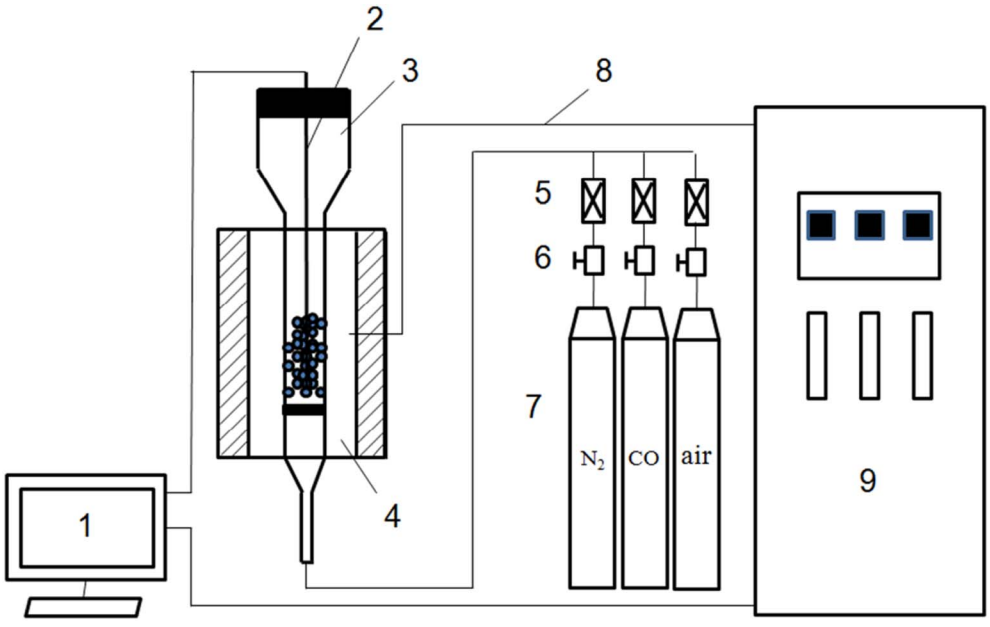

Fig. 2. Schematic diagram of the fluidized bed reaction system.

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