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A study of the impact of reduction conditions on molybdenum morphology

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ABSTRACT

The current work concerns the influence of different reduction conditions (temperature, dew point and hydrogen content as well as flow rate of reduction gas) on the morphology of molybdenum powder. The material was produced by a two-stage reduction of different sized molybdenum trioxide particles with hydrogen. The experiments were carried out in a rotary kiln. It was found that the specific surface area is mainly influenced by temperature and decreases with rising temperature. The particle size of the raw material, the dew point as well as the hydrogen content of the reduction atmosphere not only have a significant influence on the morphology of the produced molybdenum powder, but also change the impact of the temperature. The results imply that the effect of a single reduction parameter on the properties of the resulting powder always has to be seen in context with the other reaction conditions.

1. Introduction

Molybdenum, a refractory metal with a body-centred cubic crystal structure, shows excellent electric, mechanical and thermal properties. Consequently, it finds many engineering applications, for example, in high temperature furnaces, flat panel displays and solar cells. Different processing methods often require feed material with specific features such as porosity, specific surface area (SSA), final content of oxygen and grain size distribution [1–6].

Generally, pure molybdenum is produced via a powder metallurgical approach. Molybdenum trioxide (MoO_3) represents the most commonly used source material for the reduction process for molybdenum metal powder. The production of molybdenum requires two reduction steps, where hydrogen serves as reduction agent. First, MoO_3 is converted to MoO_2 at temperatures around 600–770 °C. This transformation follows the reaction path $MoO_3 \rightarrow Mo_4O_{11} \rightarrow MoO_2$ in an exothermic way. The second stage occurs at temperatures around 900–1400 °C and involves the endothermic reduction of MoO_2 to Mo [7–11].

Schulmeyer's and Ortner's studies show that the first reduction stage follows a chemical vapour transport (CVT) mechanism under all conditions, whereas the reduction of molybdenum dioxide can be dominated either by pseudomorphic or chemical vapour transport, depending on the dew point (DP). The pseudomorphic transformation occurs at a lower dew point than the CVT mechanism. Throughout the pseudomorphic transformation, the reaction interface moves from the particle surface towards the core of the grain. The product, although showing more pores and pore channels, has a similar shape to the starting material. With an increasing dew point, an intermediate gaseous transport phase (TP) emerges, resulting in the development of a new grain morphology [7,12,13].

The morphology of the molybdenum powder is mainly determined by the transformation mechanisms occurring in the second reduction step. Accordingly, desirable powder properties can be adjusted through the appropriate choice of reduction parameters [2]. The reaction mechanisms as well as the kinetics of the hydrogen reduction of molybdenum oxides were investigated in several studies [1,7,9,11,14]. Also, studies examining the effect of reduction conditions on the properties of reduced molybdenum powder have been published. Nevertheless, these studies almost exclusively focus on the impact of the temperature on the outer structure [2,15,16]. However, only little information about the impact of other reduction parameters on the surface morphology are described in literature. The focus of this study is on the influence of various reduction parameters, such as the reduction temperature, the dew point, the hydrogen content and the flow rate of the reduction gas on the morphology of molybdenum produced by hydrogen reduction of MoO_3.

2. Material and experimental procedure

2.1. Material

Pure MoO_3 sandy grade powder, supplied by Molibdenos y Metales SA, was used for the experimental process. The raw material is

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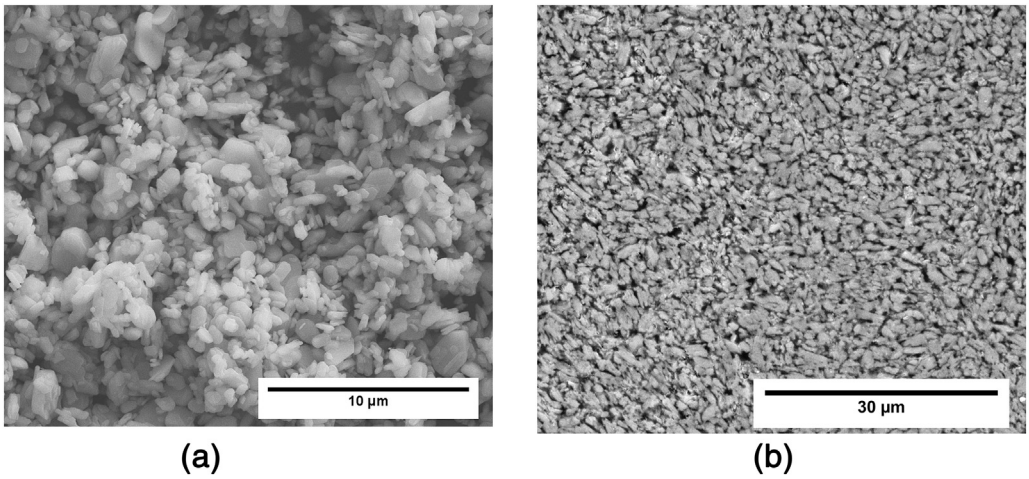

Fig. 1. SEM micrograph of the surface morphology (a) and the cross section (b) of MoO_3 used as starting material.

composed of many small rod- to acicular-shaped MoO_3 primary grains (Fig. 1). The material has a specific surface area of 2.35 m^2/g. Three different grain size fractions (63–120 µm, 120–250 µm and > 250 µm) of the feed material were used.

2.2. Experimental procedures

The reduction experiments took place in a rotary kiln (RSR 120/750/13, Nabertherm GmbH) in which a heat-resistant insert, containing the specimens, was rotated at a speed of 3 min^{-1}. The hydrogen gas was humidified by passing it through a temperature controlled bubbler system. Several gas flow meters controlled the flow rates and therefore the gas composition. Fig. 2 shows a schematic diagram of the experimental setup, compiled by the freeware ACD/ChemSketch 2016.1.1 and a database of the University of Münster. For each experimental run, 110 g of MoO_3 served as starting material. To achieve fully reduced molybdenum a reduction duration of two hours was required for each reduction stage. The determination of the required reduction duration took place in preparation to this study. A heating rate of 350 °C/h and a reduction temperature of 600 °C for the first stage of reduction was used for all experiments. The parameters dew point of hydrogen (DP), argon content in the atmosphere (Ar) and volumetric flow rate of reduction gases (VFR) were at identical settings for both reduction steps. After the transformation to MoO_2, the specimens were heated from 600 °C to the desired temperatures (850 °C, 950 °C and 1050 °C) for the second reduction step. Consequently, both reduction steps took place in one experimental run, although not in one stage. The reaction started after reaching 550 °C by switching from dry argon to reduction gas and stopped by changing the atmosphere back to argon. The samples cooled to room temperature under an argon atmosphere to prevent a reoxidation of reduced molybdenum. After reaching room temperature, the inlet was taken out of the furnace and the powder removed. For deagglomeration the specimens were grounded in a mortar and particles larger than 250 µm were extracted by sieving.

2.3. Experimental design and evaluation of results

The object of the present study was to identify the influence of the reduction temperature (T), the particle size of starting material (d50fm), the dew point of hydrogen (DP), the argon content in the atmosphere (Ar) and the volumetric flow rate of the process gases (VFR) on the morphology. The effect of the variables were investigated with a Central Composite Face design of a designed experiment (DoE). In order to gain information on the reproducibility of the experiment, three replicated centre points were included. This design with a total of 26 experiments enabled a quadratic model equation [17]. The experimental setup is given in Table 1. The reduction took place under dry (DP = − 50 °C) and humidified (DP = 25 °C as well as DP = 50 °C) atmosphere. A higher dew point could not be adjusted due to condensation of water in the gas supply line. The measured responses comprised the specific surface area.

The experimental results were evaluated with the software MODDE 11.0 (MKS Data Analytics Solutions). The fit method multiple linear regression (MLR) was applied and the model was adjusted to obtain maximum values of R^2 (accuracy of fit), Q^2 (accuracy of prediction), model validity and reproducibility [18,19]. Model terms which showed low significance on the results could be excluded to identify the parameters with the main effect on the responses. However, every single term was included to take significant linear interactions between them into account, even though they had a minor influence on the results.

2.4. Characterization methods

In order to inspect the extent of reduction, hot gas extraction

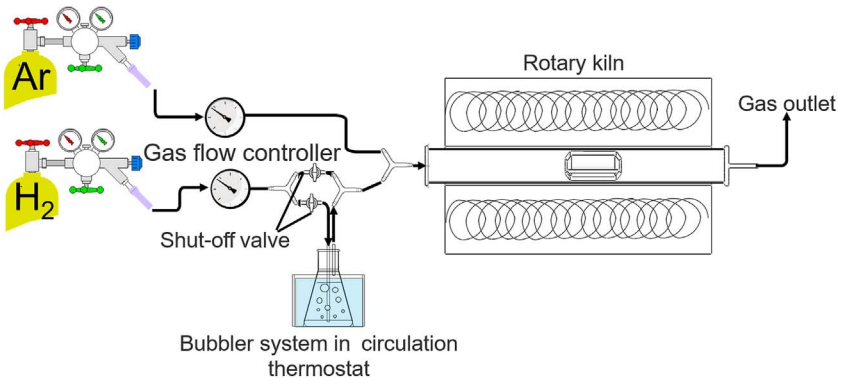

Fig. 2. Schematic diagram of the experimental apparatus for the reduction process.