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# Preparation of hierarchical porous metallic materials via deposition of microporous particles

Biao Chen, Guan-Jun Yang *, Chang-Jiu Li *, Cheng-Xin Li

*State Key Laboratory for Mechanical Behavior of Materials, School of Materials Science and Engineering, Xi'an Jiaotong University, Xi'an, Shaanxi 710049, China*

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ABSTRACT

It is the first time to report the preparation of hierarchical porous molybdenum (Mo) metal materials containing interconnected pores with a wide size range from sub-millimeter down to micrometer and nanometer scale. Microporous Mo particles were deposited in bimodal molten states, i.e. limited-molten and semi-molten state, by thermal spraying. In as-sprayed coatings, hierarchical macro/microporous structures were produced with macropores formed among solid particles and micropores remained in limited-molten particles. After annealing in a reductive atmosphere, Mo oxides inside semi-molten particles were reduced and nanometer pores were further created. Therefore, the as-received deposits exhibited multi-modal hierarchical pores with high open porosity and high specific surface area, which are promising for functional applications.



## 1. Introduction

Bio-inspired systems with bimodal or multimodal sized pores are currently of great interest due to their diverse topologies and coordination structures [1,2]. Within hierarchical porous materials, large pores provide an interconnected framework, and hence improve the diffusion or flow of fluid. Meanwhile, the fine pores in smaller sizes greatly increase the specific surface area [3]. This unique structure brought many superior properties and potential functional applications to hierarchical porous materials [1–3]. Due to the high strength, high conductivity and high catalytic activity of metallic matrices, hierarchical porous metallic materials are of great importance for using as fuel cell electrodes, filters, catalysts and catalyst supports [4–7].

Up to date, varieties of methods have been developed to prepare hierarchical porous metallic materials, such as template method [8–10], chemical vapor deposition [11] and sol-gel method [12]. Among them, the template method is an efficient way to prepare hierarchical porous metallic materials with tunable structures and pore textures. However, this method is complicated, costly and always involves in highly toxic substances, which hinders the application in large-scale production [8,13]. Herein, this paper reported a template-free method to prepare hierarchical porous metallic materials with multi-modal sized pores through flame spraying assisted with annealing. The approach was simple, cheap and environment friendly to fabricate hierarchical porous molybdenum metal. In principle, it was also applicable to fabricate hierarchical porous metallic materials for other metal and alloy systems with reducible metal oxides.

## 2. Experimental

Commercially available microporous Mo metal powders (Xinke Co., Wuxi, China) with a particle size of 75–200 μm were used as the feedstock material. A commercial flame torch was used to generate spray particles for build-up of Mo deposits. The powder feed rate was fixed at ~5 g/min. A neutral flame was applied with an acetylene flow rate of 400 L/h. The torch traverse speed and spray distance were fixed to 30 mm/s and 40 mm, respectively. The as-sprayed Mo deposit was annealed by placing samples in a corundum crucible in a hydrogen gas ($H_2$) atmosphere. The target temperature was 1000 °C and holding time was 1 h. A detailed description of the process could be found elsewhere [14].

The surface morphology and cross-section microstructure of the Mo particles and deposit samples were characterized by scanning electron microscopy (SEM, VEGA II-XMU, TSCAN, Brno, Czech Republic). Accessary energy dispersion spectrum (EDS) analysis was applied to examine element composition. The material phases were identified by x-ray diffraction (XRD). The XRD

* Corresponding authors.
*E-mail addresses:* ygj@mail.xjtu.edu.cn (G.-J. Yang), licj@mail.xjtu.edu.cn (C.-J. Li).

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samples for as-sprayed and as-annealed materials were obtained by removing the deposits from the substrate and grinding them to powders. To protect the porous structure, the Mo deposits were infiltrated by adhesives before sample cutting and polishing. The average apparent macroporosity of the deposit was measured from ten polished cross-sectional images at a magnification of 200. The average microporosity and nanoporosity were estimated from the equation $P=(1-P_{macro})\cdot f\cdot P_{particle}$, where P is the microporosity or nanoporosity, $P_{macro}$ is the macroporosity, and $f$ and $P_{particle}$ are the fraction and porosity of semi-molten or limited-molten particles, respectively. $P_{particle}$ was also measured from images at the magnification of 200.

## 3. Results and discussion

Fig. 1a shows the morphology of raw microporous Mo particles. It can be seen that the particles consisted of small Mo granules with a diameter of several micrometers. Interconnected micropores extended tortuously into the powder among the granules as shown in the inset of Fig. 1a. Fig. 1b shows the XRD patterns of raw Mo powder, as-sprayed deposit and the annealed material. An oxide mixture of $MoO_2$, $MoO_3$ and $Mo_4O_{11}$, formed in the as-spared Mo deposit, indicating the deposit as a Mo oxide/Mo composite. After post-annealing, the peaks corresponding to Mo oxides generally disappeared, indicating the annealed deposit as metallic Mo material. The phenomena of oxidization and complete reduction of Mo oxides are in agreement with the previous study using dense Mo as raw material under similar processing conditions [14].

Fig. 2 shows the surface morphology of the as-sprayed Mo deposit. The macropores in sub-millimeter scale among the solid particles can be obviously observed in Fig. 2a. The formation mechanism of macropores has been clarified as the shielding effect of

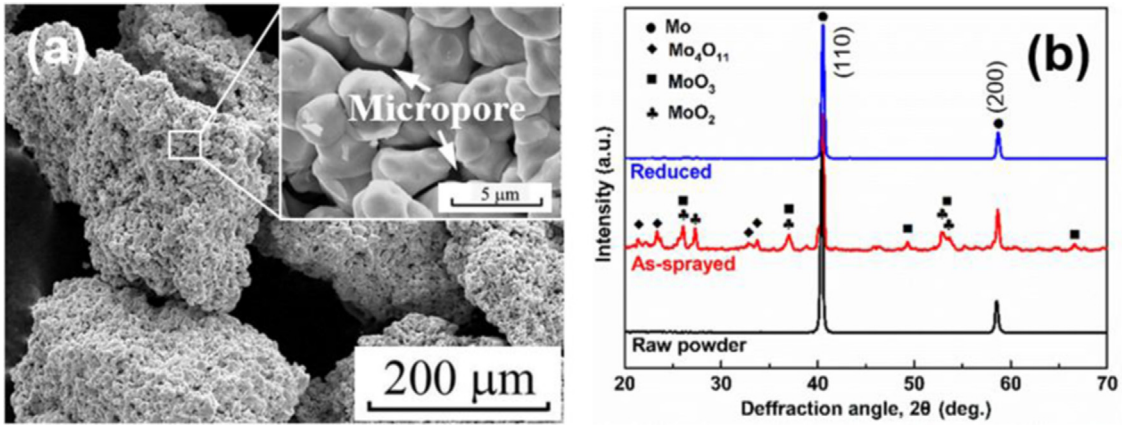


**Fig. 1.** Morphology of raw Mo powder (a) and XRD patterns (b) of raw powder, as-sprayed deposits (as-sprayed) and reduced materials (reduced).

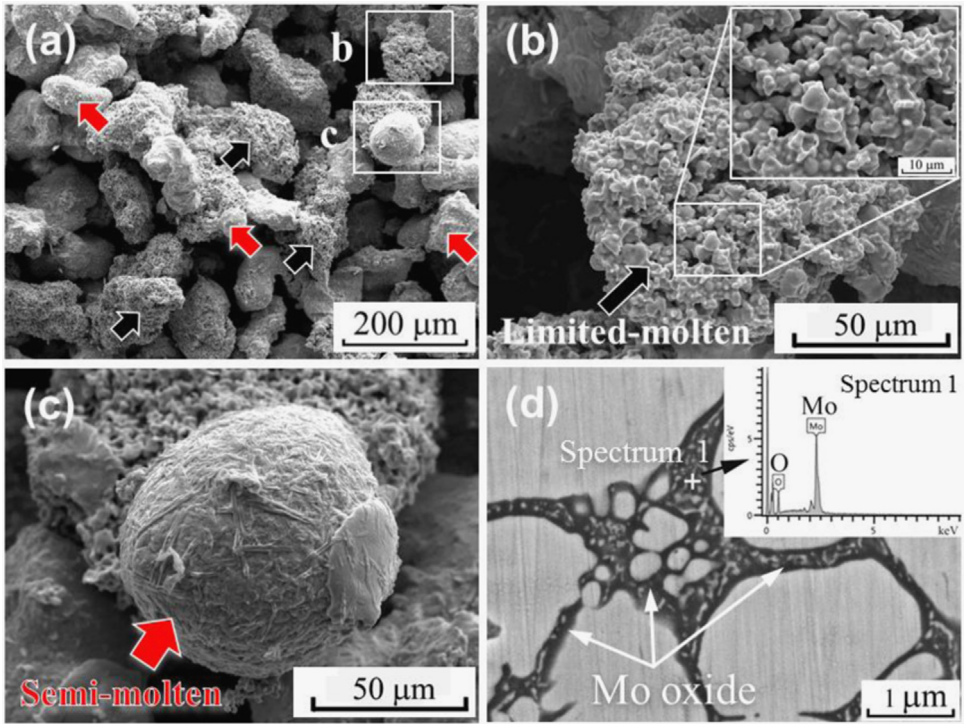


**Fig. 2.** Surface morphology (a-c) and cross-section microstructure (d) of as-spayed Mo deposit. (a) A general view. (b) A typical limited-molten particle. Inset shows high-magnification view of the limited-molten particle. (c) A typical semi-molten particle. (d) High-magnification view of a semi-molten particle. Inset shows EDS analysis of indicated point.