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Preparation of hierarchical porous metallic materials via deposition of microporous particles

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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

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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

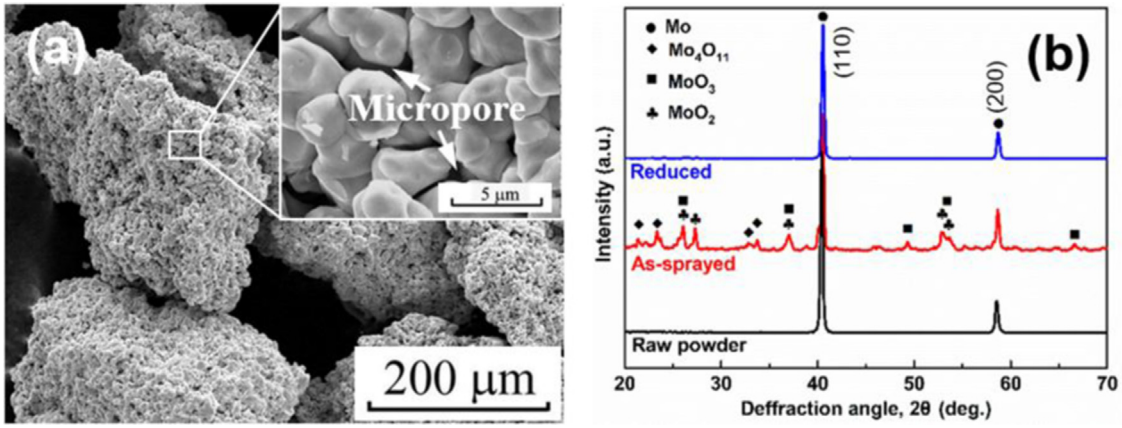

Fig. 1. Morphology of raw Mo powder (a) and XRD patterns (b) of raw powder, as-sprayed deposits (as-sprayed) and reduced materials (reduced).

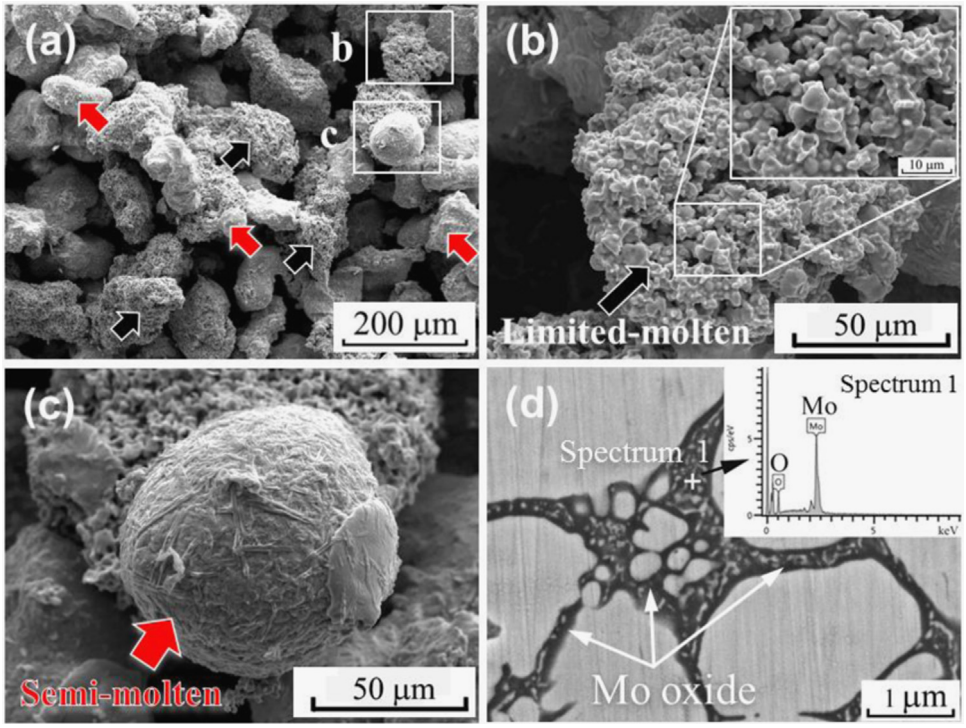

Fig. 2. Surface morphology (a-c) and cross-section microstructure (d) of as-spayed Mo deposit. (a) A general view. (b) A typical limited-molten particle. Inset shows high-magnification view of the limited-molten particle. (c) A typical semi-molten particle. (d) High-magnification view of a semi-molten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

un-molten spray particles in our previous studies using dense metal powders [14–16]. In this study, it was interestingly observed that the deposited porous particles exhibited two distinguishable molten states. Some limited-molten particles with a molten degree of nearly zero, presented a similar morphology (Fig. 2b) to that of the raw particles (Fig. 1a). The remained micropores can be clearly observed in the inset of Fig. 2b. Meanwhile, other particles exhibited near-spherical shapes with closed surfaces (Fig. 2c), indicating a semi-molten state [14] prior to deposition. The bimodal molten states of spray particles, i.e. limited-molten state and semi-molten state, could be achieved through controlling the size distribution of raw powders [17,18]. From the cross-section microstructure of a semi-molten particle (Fig. 2d), Mo oxides with gray contrast filled in the space among small Mo granules with white contrast. The combination of EDS analysis (inset of Fig. 2d) and XRD patterns (Fig. 1b) clearly identified the Mo oxide phases.

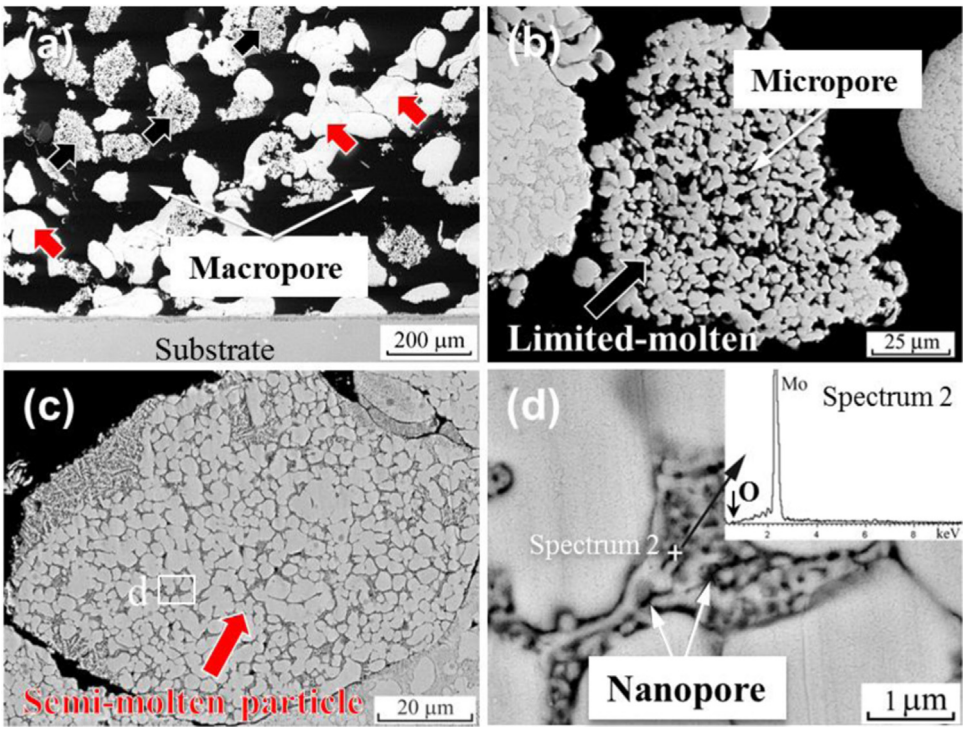

Fig. 3. Cross-section microstructure of hierarchically porous Mo material after annealing. (a) A general view. (b) A typical limited-molten particle. (c) A typical semi-molten particle. (d) A typical semi-molten particle. (d) High-magnification view of the box in (c) shows newly formed nanopores in semi-molten particles. Inset shows EDS analysis of indicated point.

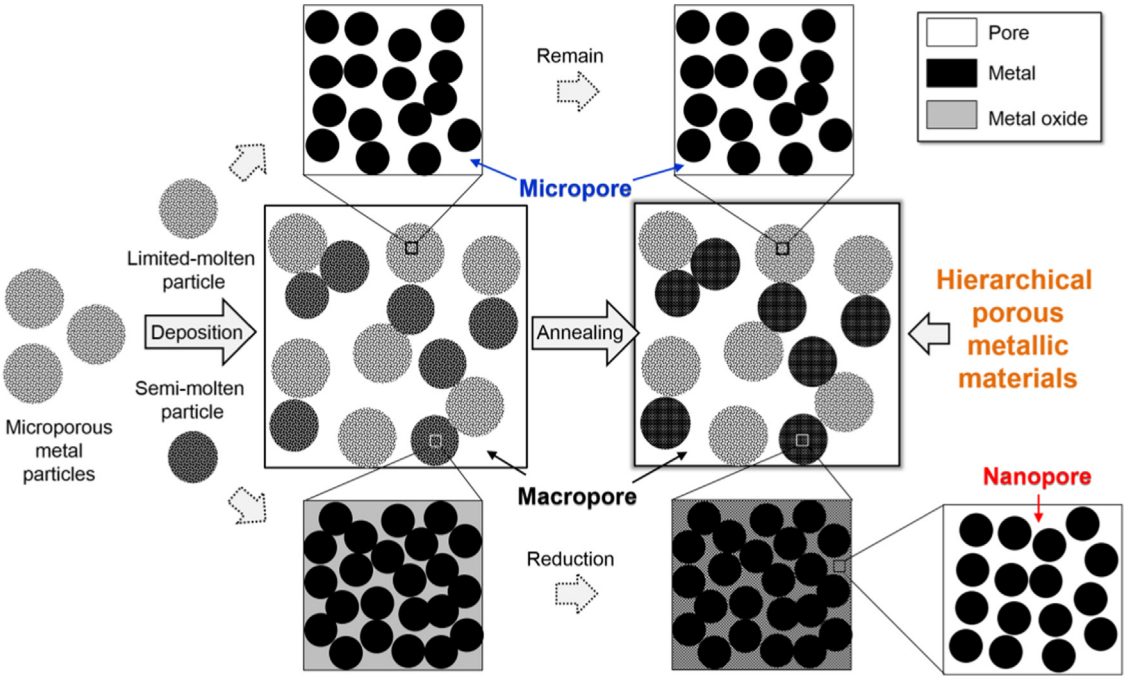

Fig. 4. Schematic formation process of hierarchical macro/micro/nanoporous metal materials via flame spraying and annealing.

After annealing, there was little structure change observed from the surface morphology. The microstructure of annealed deposit was thus observed from the cross-section view at different magnifications, as shown in Fig. 3. The areas appeared in a black contrast, corresponding to the infiltrated resin, represent pores in the deposit. Interconnected macropores and micropores were clearly observed (Fig. 3a), agreeing with the surface morphology of as-sprayed deposit (Fig. 2a). Fig. 3c shows a typical semi-molten particle after annealing. From a close view (Fig. 3d), it was observed that there were numerous tiny pores with a diameter or neck size of ~100 nm. The nanopores in black contrast distributed among the infiltrated particles in whiter contrast (Fig. 3d). The EDS analysis (inset of Fig. 3d) suggested low oxygen concentration in the nanopores. The combination of SEM observations (Fig. 2d and Fig. 3d), XRD patterns (Fig. 1b), and EDS spectra (Insets of Fig. 2d and Fig. 3d) proved the complete reduction from Mo oxides to metallic Mo. It was reported that during the chemical reaction between metal oxides and H_2 at a high temperature, the loss of oxygen atoms created fine vacancies in the produced metallic material [19]. Therefore, the formation of nanopores was due to the reduction of Mo oxides to metallic Mo in semi-molten particles. The newly produced nanopores were also open to macropores, because of the chemical reaction between Mo oxides and H_2 gas. Moreover, the total porosity was measured as 58%, resulted from $50 \pm 5\%$ in macropores, $5 \pm 1\%$ in micropores, and $3 \pm 1\%$ in nanopores. Due to the fine size of micropores and nanopores, the surface area of the porous material can be noticeably improved [20].

Fig. 4 schematically shows the formation process of hierarchical porous structure developed in this study. As porous metallic particles with a wide size range are used for flame spraying, limited-molten and semi-molten particles are simultaneously produced and then they are stacked to a deposit. Interconnected macropores among particles and micropores inside limited-molten particles are produced in the as-sprayed metal oxide/metal composite deposit (Fig. 4). Meanwhile, the micropores in raw particles are filled with metal oxides in semi-molten particles. After annealing, tiny nanometer pores are further produced in the semi-molten particles because of the reduction of metal oxides. The bimodal macro/micropores in as-sprayed deposits is still remained. As a result, the whole deposit exhibits a multimodal pore-sized porous structure ranging from sub-millimeter down to micrometer and nanometer scale. The macropores dominantly contribute to a high porosity, while fine micropores and nanopores provide high surface areas. Except for Mo, many other reducible metals, such as Fe, Ni and Cu, could form metal oxides under thermal processes in atmospheric environment and could be further reduced by post annealing [17,18]. Therefore, it was expected that various hierarchical porous metallic materials, which are promising for using as catalysts/catalysts supports, filters and electrodes, can be prepared from the present method.

4. Conclusions

In summary, this study reports a novel method to produce hierarchically porous Mo deposits by flame spraying assisted with annealing. A bimodal porous structure containing macropores and micropores can be produced in as-sprayed Mo oxide/Mo composite deposit. Micropores are originated from the raw pores in limited-molten particles. After annealing, nanopores are further created inside semi-molten particles through the reduction of oxides to metallic Mo. Consequently, the deposit exhibits an open and hierarchical macro/micro/nanoporous structure. The process is simple and promising for the large-scale production of hierarchical porous metallic materials for functional applications.

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