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Preparation of nanoporous tungsten by liquid metal dealloying

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ABSTRACT. Liquid metal dealloying is the novel technique for generating porous structure from less noble metals. In this study, nanoporous tungsten was prepared by dealloying in a metallic melt from a tungsten-nickel precursor with different atomic compositions. All W-Ni precursors were immersed in Mg melt, and the dealloying temperature and time to obtain fully porous tungsten was studied. The results identified by X-ray diffraction (XRD) with Cu-Kα radiation show that obtained porous powder is single W. Microstructures were observed by scanning electron microscopy (SEM) shows that obtained powder has fully nanoporous structure. The ligament size was calculated from the image and the average pore, pore volume and specific surface area were examined by the BET method. According to the author's knowledge, nanoporous tungsten was successfully prepared by liquid metal dealloying for the first time.

KEYWORDS. dealloying; nanoporous tungsten, metallic melt, mixing enthalpy, ligament.

1. INTRODUCTION

Nanoporous metals offer promising applications in fuel cells, catalysis, biosensors and photonic device because of their nanoporous structures and high specific surface areas [1]. Dealloying in aqueous solution is the main technique to prepare nanoporous metals, such as Au, Pt, Pd, Ag and Cu [2,3]. Dealloying refers to the selective dissolution of one or more active components out of homogeneous alloy precursor [4].

Tungsten is an outstanding metal with high melting point, large electric resistance, high hardness and excellent high temperature mechanical properties. Therefore, nanoporous tungsten provide functional applications including electrocatalytic cathodes in photoelectrochemical cells for renewable and sustainable solar energy conversion, electrode of fuel cell and a crucial component of dispenser cathodes. Unfortunately, tungsten is the most appropriate example of a metal not meeting the requirements for nanoporosity evolution by chemical dealloying.

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For that reason, we studied a novel dealloying in metallic melts to generate nanoporous tungsten. Liquid metal dealloying (LMD) which makes the formation of nanoporous structure possible even for less-noble metal uses a metallic melt, instead of an aqueous solution [2]. The liquid metal is chosen to have a negative mixing enthalpy with the dissolving component(s) and a positive mixing enthalpy with the remaining component [5]. In this work, we report the dealloying reaction design, preparation of precursor and characterization of nanoporous tungsten.

2. Experimental Procedure

For this liquid metal dealloying method, a metallic melt that slightly reacts with tungsten should be first selected. In this experiment, Mg was selected as a metallic melt because it is immiscible with W and miscible with Ni according to the mixing enthalpies, as is reported in Ref. [6].

For the precursor, W should be alloyed with an element such as Ni, Co that can be easily dissolved in Mg melt. Reaction design of liquid metal dealloying is shown in Fig. 1.

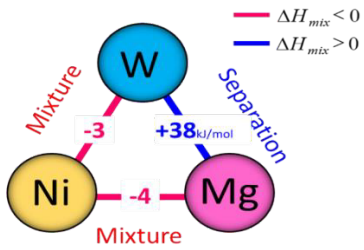


Figure 1. Reaction design of LMD

A schematic illustration for the fabrication process is shown in Fig. 2. Binary W-Ni precursor alloys with different compositions of $W_{20}Ni_{80}$, $W_{40}Ni_{60}$ and $W_{60}Ni_{40}$ (at.8%) were prepared by arc melting using high purity (99.99 mass%) starting materials in an Ar atmosphere purified with a Zr getter. Arc melted buttons were casted by tilt casting for more homogeneous structure. Resulting ingot was cut into slices roughly 5x2x15mm. About 50 g of pure Mg (99.99 mass%) as a metallic melt was inductively heated in a carbon crucible at 973K, 1073K and 1173K and the W-Ni slices were immersed in a liquid Mg for 10, 20 and 30 min. When a W-Ni precursor is immersed in a Mg melt, only Ni atoms dissolve in the Mg melt, and the remaining W atoms are expected to form a porous structure. [7]. After immersion, the samples were etched by the 3 mol/l hydrochloric acid solution for 1hr to 12 hours depending on tungsten concentration of precursor at room temperature. Then the hydrochloric acid aqueous solution was filtrated and the porous powder was washed with distilled water until neutral and dried in an oven at 393K for 1 hr.

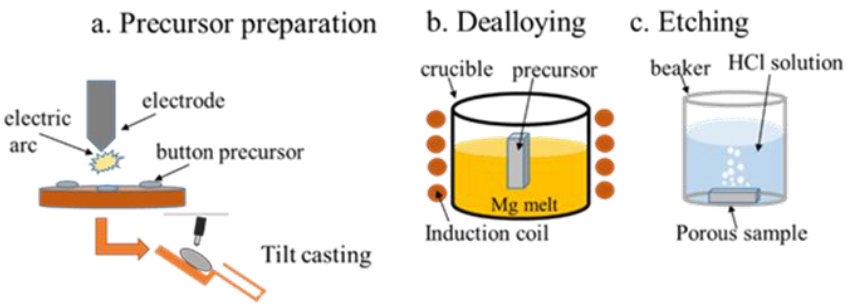
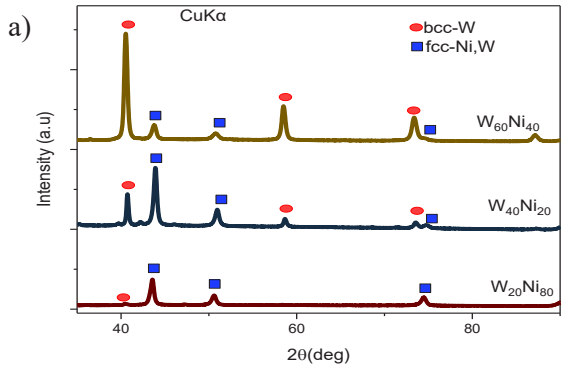


FIGURE 2. Schematic diagram of the fabrication process of nanoporous tungsten by the dealloying method

The phase analysis was characterized by X-ray diffraction with CuαK radiation (XRD, Rigaku/Ultima IV diffractometer). The microstructure was characterized by scanning electron microscopy (SEM, Zeiss Ultra 55). The ligament size of nanoporous tungsten was calculated from the image by measuring the shortest distance across the ligament [8] and the average pore, pore volume and specific surface area were examined by the BET method.

3. RESULTS AND DISCUSSION

3.1. **Characterization of the W-Ni Precursor.** The XRD pattern of the $W_{20}Ni_{80}$, $W_{40}Ni_{60}$ and $W_{60}Ni_{40}$(at.%) precursor alloys in Fig 3.a) verifies the presence of the Ni-W solid solution and bcc-W phases. Fig 3.b) shows the SEM images of W-Ni precursors and results of the EDX mapping for W and Ni distribution of the $W_{20}Ni_{80}$ alloy precursor. It is clear from the EDX map that the precursor is homogeneous and composed of $W_{20.18}Ni_{79.82}$. The XRD pattern and EDX results revealed that fabricated precursor is proper for target composition.



b)

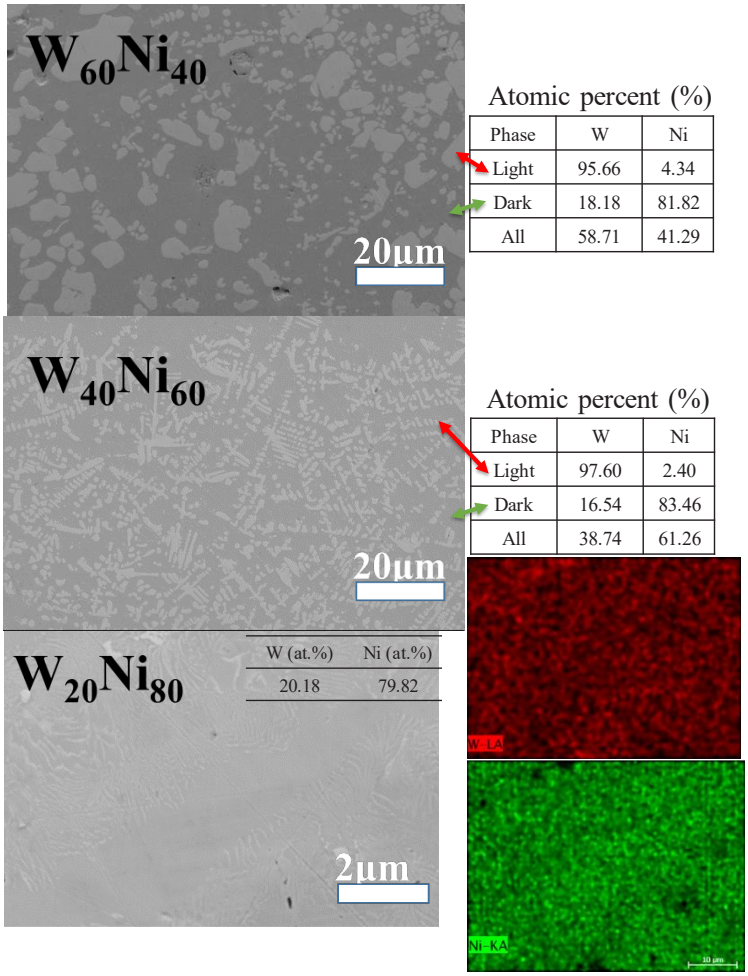


FIGURE 3. a) XRD pattern b) SEM image of the W-Ni alloy precursors and EDX mapping results of $W_{20}Ni_{80}$.

3.2. **Characterization of $W_{20}Ni_{80}$ alloy precursor after LMD.** Fig. 4. shows the SEM image of cross-section composed of three different layers after immersion in a Mg melt at 1073K for 10 min. The top layer is considered to be the Mg melt, the medium layer is dealloyed region and the bottom layer is initial precursor layer in Fig. 4.a). These three layers were characterized by the composite in hydrochloric acid aqueous solution, because of the good corrosion resistance of bcc-W and the poor corrosion resistance of hcp-Mg. The SEM image and the XRD patterns in Fig. 4. shows that Ni element of W-Ni precursor dissolves into the Mg melt and remaining bcc-W self-organizes nanoporous structure. Fig3.a) verifies the presence of the Ni-W solid solution and bcc-W phases. Fig3.b) shows the SEM images of W-Ni precursors

and results of the EDX mapping for W and Ni of the W20Ni80 alloy precursor. It is clear from the EDX map that the precursor is homogeneous and composed of W20.18Ni79.82. The XRD pattern and EDX results revealed that fabricated precursor is proper for target composition, because of the good corrosion resistance of bcc-W and the poor corrosion resistance of hcp-Mg. The SEM image and the XRD patterns in Fig 4. show that Ni element of W-Ni precursor dissolves into the Mg melt and remaining bcc-W self-organizes nanoporous structure.

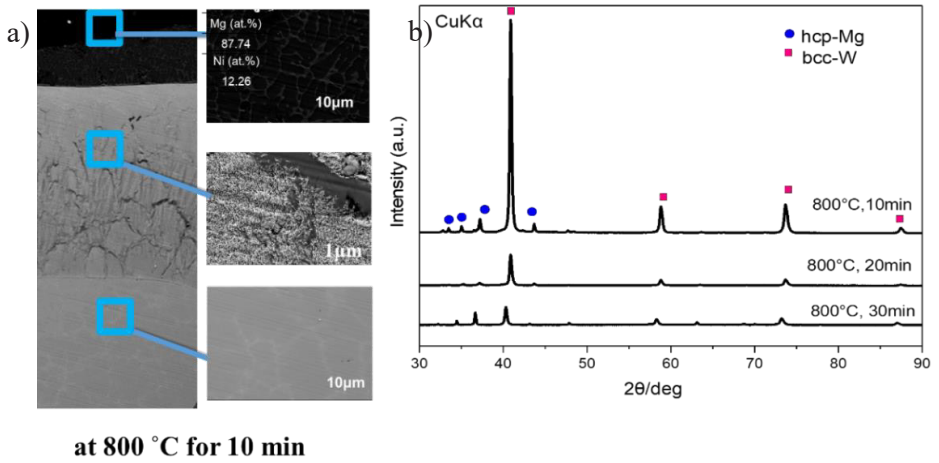


FIGURE 4. a) SEM image and b) XRD patterns of the W-Ni alloy after immersion in Mg melt

3.3. **Characterization of Nanoporous Tungsten.** Fig. 5. shows SEM images of the dealloyed products, which were synthesized by dipping the precursor in a Mg melt at different temperatures for different time to complete the reaction, removing the Mg-Ni phase in HCl solution and then washing and drying. Nanoporous tungsten with ligament size 80~130nm was found. The SEM images in Fig 5. show that when the time and temperature increased, ligament size of porous tungsten was increased as well. The XRD curve in Fig.5 shows that porous product is pure tungsten.

TABLE 1. np-W characteristics from BET.

Average pore size, (nm)	Porosity, (%)	Specific surface area, (m^2/g)
48	53	5

The average pore size, porosity and specific surface area are measured by BET method and summarized in Table I. Nanometals are a group of porous metals which have large porosities greater than 40% and pore diameters of 1-100nm [9]. Nanoporous tungsten with average pore size 48nm and porosity 53% was prepared by the liquid metal dealloying.

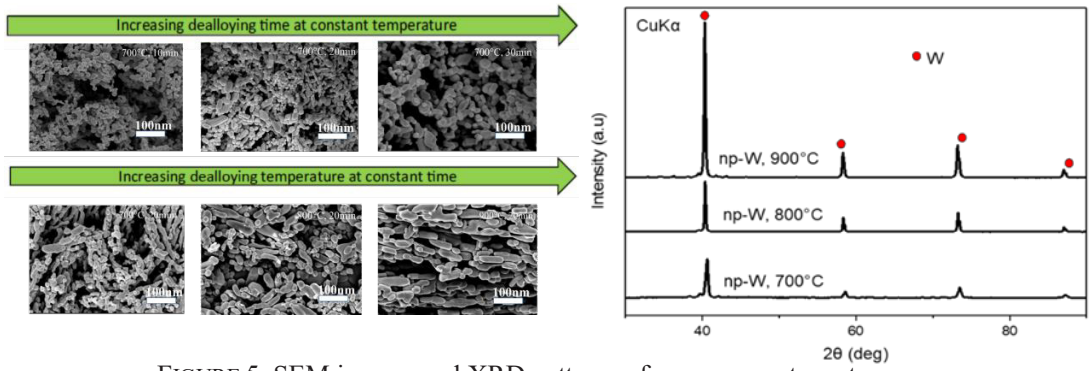


FIGURE 5. SEM images and XRD patterns of nanoporous tungsten

4. CONCLUSION

In summary, the nanoporous tungsten was prepared for the first time, using a liquid metal dealloying technique. Arc melted $W_{20}Ni_{80}$ precursor consists of fcc-Ni,W solid solution with little W phase. Porous W with the ligament size 80~130nm and specific surface area ~5m^2/g was successfully obtained.

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