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Optimizing niobium dealloying with metallic melt to fabricate porous structure for electrolytic capacitors

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Abstract—The transition behavior from a Nb–Ni precursor to porous Nb and the coarsening of ligaments by a dealloying reaction in a Mg melt are investigated. Based on these results, the kinetics of the reaction are discussed. When a $Nb_{25}Ni_{75}$ (at.%) disk was immersed in a Mg melt, the Ni content decreased the most at the surface of the disk and less so towards the interior of the disk. In this disk, it was found that transition layers of body-centered cubic-Nb and Ni_6Nb_7 formed. These transition layers grew, following a parabolic law, and the activation energy of such growth was close to values reported for the diffusion of solute atoms in liquids, suggesting that diffusion of Ni in the Mg melt was the rate-controlling process of the dealloying reaction. The ligament size depended on time and temperature, following a power law with an exponent of 4, suggesting that surface diffusion was a key part of coarsening. These results agree well with those reported for conventional dealloying in an aqueous solution. Based on the kinetics analyses, the dealloying conditions were optimized to maximize the specific surface area, allowing a Nb electrolytic capacitor to be produced with a maximum mass-specific capacitance of 650,000 μFV g^{-1}, about three times larger than the highest value previously reported.

Keywords: Dealloying; Porous material; Nb electrolytic capacitor; Nanostructure

1. Introduction

Improving electrolytic capacitors is important for further miniaturization of small electronic devices. Currently, tantalum is widely used for electrolytic capacitors because it has a high specific capacitance and unique operating characteristics at low frequencies and high currents [1–3]. Recently, niobium has been considered as a promising alternative to tantalum because of its lower cost and specific gravity, higher natural abundance, and the higher relative permittivity of Nb_2O_5 ($\varepsilon = 41$) [4,5]. The capacitance of an electrolytic capacitor can be increased by increasing the specific surface area S of the porous anode pellets. However, the capacitance of porous anodic pellets is limited by their conventional fabrication process: sintering sub-micrometer tantalum/niobium powder at high temperature. During sintering, the surface area of these pellets inevitably decreases as the size of ligaments grows to the microscale. If nanoporous Nb could be prepared without sintering, its surface area and thus its capacitance should improve greatly [6,7].

A well-known process for preparing nanoporous metals is dealloying in aqueous acid/alkali solutions. In this process, one or more alloy elements in an alloy precursor are selectively dissolved into an acid/alkali aqueous solution, and sometimes the reaction is controlled electrochemically. This method can be used with noble metals such as Au, Pt, Pd and Cu, and with base metals that have higher standard electrode potentials, such as Ni, Fe and Co [8–12]. This method cannot be used with niobium, because niobium oxidation disturbs the foaming, which creates the porosity in the product. Recently, the present authors' group developed a new dealloying method, which used a metallic melt as the dealloying medium instead of an aqueous solution [13]. This method allows development of a three-dimensional nanoporous metals not only with noble metals, but also with base metals such as α-Ti, a β-Ti alloy, Fe, Cr and a ferritic stainless steel, using alloy precursors of Ti–Cu, (Ti, Zr, Cr)–Cu, Fe–Ni, Cr–Ni and (Fe, Cr)–Ni, respectively [13–15]. The nanoporous metals produced using a metallic melt are structurally similar to those prepared by conventional (electro)chemical dealloying, and the dealloying process also preserves the precursor shape fairly well. The present authors believe that this method could produce nanoporous Nb pellets directly from precursor pellets without sintering, which grows the ligaments and

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thus reduces the surface area. To confirm this concept, the dealloying method was used to fabricate porous Nb anode pellets using a Nb–Ni alloy precursor and a Mg melt; these pellets were then used to fabricate an electrolytic capacitor that exhibited improved mass-specific capacitance [16]. To further increase the capacitance, the porous structure should be optimized to increase the specific surface area by decreasing the ligament size. The present study investigated the kinetics of the formation and coarsening of the porous Nb. Based on these kinetics analyses, the dealloying conditions were optimized and porous Nb with greater specific surface area was obtained, further increasing its mass-specific capacitance to 650,000 μFV g^{-1}.

2. Experimental procedure

Binary Nb–Ni alloy ingots with nominal compositions of $Nb_{25}Ni_{75}$ and $Nb_{40}Ni_{60}$ (at.%) were prepared by arc-melting Ni (99.9 mass%) and Nb (99.99 mass%). Samples with two different shapes (thick, disk-shaped samples and thin, ribbon-shaped samples) were prepared from the ingots for these experiments.

The disk sample was thick enough to have transition layers, making it suitable for investigating the kinetics of the transformation from the Nb–Ni alloy precursor to the final porous Nb by measuring the thicknesses of the transition layers. To simplify discussion of the transformation behavior, for this experiment $Nb_{25}Ni_{75}$ (at.%), which consists of a single phase of $NbNi_3$, was selected. A rod of $Nb_{25}Ni_{75}$ with a diameter of 8 mm was prepared by tilt casting using a Cu mold in an Ar atmosphere; to homogenize the rod, it was annealed at 1273 K for 8 h. The rod was then cut into disks with thicknesses of 1 mm. The surface of the disk was mechanically polished with #120–1200 emery paper.

The ribbon sample was thin enough to fully dealloy in a short time; the time for completed dealloying was considered to be negligible compared with the time needed for ligament coarsening. Thus, the ribbon sample was suitable for investigating the kinetics of the ligament coarsening by observing ligament growth over time. However, $Nb_{25}Ni_{75}$ has a high melting point T_m of ~1671 K, making it unsuitable for melt spinning when fabricating a ribbon-shaped precursor. Given this limitation, a ribbon sample of $Nb_{40}Ni_{60}$ was prepared, an excellent glass former with a T_m of ~1451 K, a width of ~10 mm and thickness of 70 μm. $Nb_{40}Ni_{60}$ glassy ribbons are advantageous for mass fabrication compared with $Nb_{25}Ni_{75}$ disks, making them suitable as precursors for Nb capacitors. However, $Nb_{40}Ni_{60}$ glassy ribbons in a Mg melt will crystallize into multiple phases, including $NbNi_3$ and Nb_7Ni_6, because the dealloying temperature is higher than the crystallization temperature; thus, this ribbon sample was not used to investigate the transformation from the Nb–Ni alloy precursor to porous Nb. The $Nb_{40}Ni_{60}$ ribbon was cut into increments of 5 mm along the length.

Dealloying was performed by immersing the precursor in molten Mg, contained in a carbon crucible at a fixed temperature between ~1023 K (the lower limit for the dealloying reaction) and ~1173 K (the upper limit because of the severe vaporization of the Mg melt above this temperature) in a He atmosphere, injected after lowering the pressure to $\sim 2 \times 10^{-3}$ Pa. The melt temperature was controlled to ±2 K, and the immersion time was 60–1200 s. After this dealloying treatment, any Mg adhering to the specimens was etched using an aqueous solution of 1M HNO_3. After removing each specimen from this bath, it was carefully washed with deionized water and methanol and then dried in air. To observe the sample morphology after dealloying, each dealloyed disk was embedded in resin, mechanically

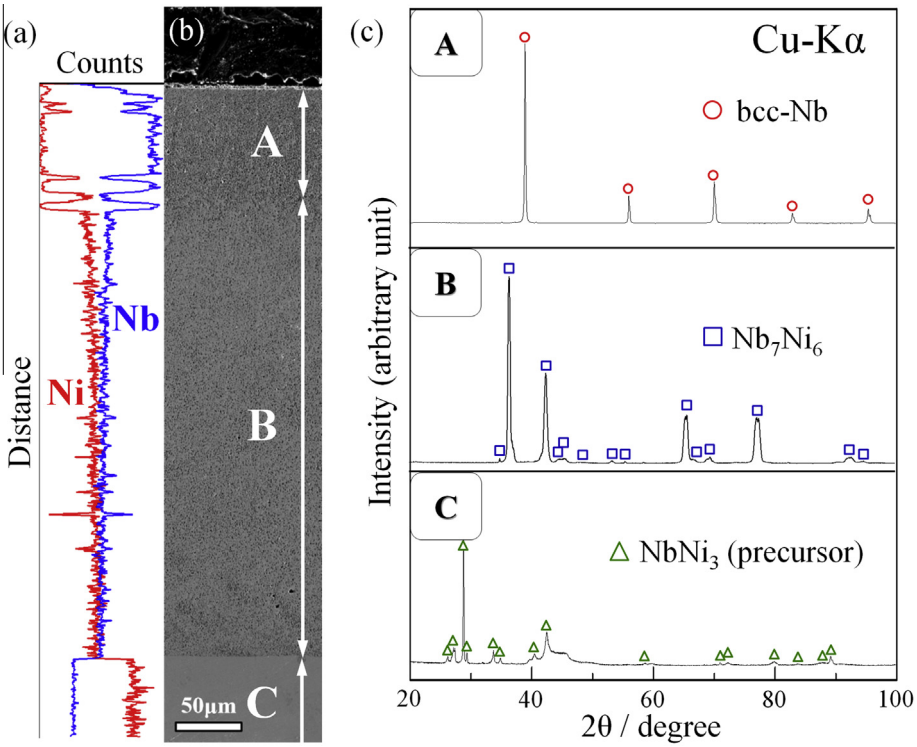

Fig. 1. (a) Concentration profile of Nb and Ni, (b) cross-sectional SEM image and (c) XRD pattern of the A, B and C layers for the $Nb_{25}Ni_{75}$ disk sample after dealloying in a Mg melt at 1123 K for 120 s.