Effects of pulse voltage on the formation of nanoporous Ti oxides by dealloying amorphous TiCu alloy

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Abstract. In present study, we prepared nanoporous Ti oxides by potentiostat and pulse dealloying TiCu amorphous alloy in HNO\textsubscript{3} solution. The influence of applied voltage on the morphology was investigated by SEM. The mechanism of dealloying was also discussed. A multilayer nanoporous structure was fabricated using pulse dealloying. The ideal nanoporous structure with mean pore diameter of about 50-100 nm and mean pore wall thickness of about 50 nm was obtained using pulse dealloying with initial voltage of 1.0 V and pulse size of 0.4 V. The static currents for pulse dealloying are higher than those for potentiostat dealloying under the same initial potentials. The nanoporous surface is mainly composed of TiO, Ti\textsubscript{2}O\textsubscript{3} and TiO\textsubscript{2}.

1. Introduction
Titanium dioxide (TiO\textsubscript{2}) is one of the important semiconductor materials which is widely used as an efficient photo-catalyst, because it is chemically and biologically inert, photo-catalytically stable, commercially available and inexpensive, and environmentally friendly [1-3]. The valence band (VB) of TiO\textsubscript{2} (versus natural hydrogen electrode) lies at deep levels and photo-generated holes have strong enough oxidizing power to create OH radicals, which decompose most organic pollutants [4]. Position of its conduction band (CB) is also high enough to reduce oxygen molecules adsorbed on the surface [5]. An important requirement for high TiO\textsubscript{2} electro catalytic efficiency is a large surface area which enhances electron transfer. Nanostructured TiO\textsubscript{2} materials, with a typical dimension less than 100 nm, have recently emerged. Such materials include spheroidal nanocrystallite and nanoparticles together with forming porous film [6-9], nanotubes[10,11], nanosheets[12], and nanofibers[13]. Recently, nanoporous metallic materials have received increasing attention due to large surface-to-volume ratio, light weight, excellent electrical/thermal conductivity and quantum size effect [14]. They can be widely used in catalysis, biofiltration, surface enhanced Raman scattering, surface plasmon resonance, sensor, drug delivery, etc.

Dealloying, as also called the selective corrosion, is a process that the active elements in the original alloy system are dissolved in the electrolyte solution, but the inert elements reserve in the

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alloy and re-assemble into the porous structure. Due to the strict requirements for the starting alloys of dealloying, only limited crystalline alloy systems have been demonstrated to form uniform nanoporous structures, such as Ag-Au [15], Zn-Au [16], Al-(Au, Ag, Pd, Cu) [17], Cu-Au [18], Si-Pt [19], Cu-Pt [20], Mn-Cu [21], Au-Pd [22], etc. In comparison with crystalline alloys, amorphous alloys are considered as good starting alloy for dealloying due to their monolithic phase with a homogeneous composition and structure down to subnanoscale [23, 24]. There are several attempts to synthesize nanoporous metals using amorphous alloy as the starting alloy [25, 26, 27]. In our previous work, nanoporous structure was synthesized on the surface of Ti-Cu amorphous alloy in nitric acid solution [28]. However, it is difficult to fabricate multilayered nanoporous structure on Ti and Ti alloys using traditional electrochemical etching because of their self-passive properties. In present study, we investigated the effect of pulse voltage on the formation of nanoporous Ti oxides by dealloying the amorphous TiCu alloy.

2. Experiments
The Ti$_{30}$Cu$_{70}$ (nominal atom percent) amorphous alloy ribbons with width of 2 mm and thickness of several 10 μm were prepared by melt spinning. The amorphous alloy ribbons were cut into 40-50 mm in length. After cleaned in deionized water by ultrasonic cleaner, the ribbons were subjected to dealloying process in 30 wt% HNO$_3$ solution at 70 ℃ using a Gamry Reference 600 electrochemical workstation. A three-electrode electrochemical configuration was employed: a Ti$_{30}$Cu$_{70}$ amorphous alloy ribbon working electrode, a saturated calomel electrode (SCE) as reference electrode and a platinum mesh as counter electrode. The morphology of nanoporous structure was investigated by Hitachi S4800 Scanning Electron Microscope (SEM). The chemical composition of the nanoporous sample and valence state of elements were characterized by X-ray Photoelectron Spectroscopy (XPS).

3. Results and discussion
Fig. 1 shows the microstructure of nanoporous surface prepared by potentiostat dealloying in 30 wt% HNO$_3$ solution for 10800 s. The insets in the blue square are the low magnification images. Fig.2 shows the corresponding I-t curves. Lots of shallow pits are observed on the surface of sample subjected to etching under 0.5 V voltage (Fig. 1(a)). Nanoporous structure is obtained for the etching under 1.0 V voltage, as shown in Fig. 1(b). When the voltage increases to 1.5 V, the nanoporous structure is ruined (Fig. 1(c)). The I-t curves exhibit similar shape: decreasing sharply, and then increasing slowly, finally reach the static current after about 5000 s. The static current of 1.0 V etching is slightly higher than that of 0.5 V etching, and much lower than that of 1.5 V etching. Three events would occur when applying anodic potential on the TiCu alloy in HNO$_3$ solution: removing the Cu element, forming oxides film and electrochemical polishing (indeed, the electrochemical polishing includes the corrosion of Ti, Cu and their oxides). The HNO$_3$ solution can dissolve Cu and its oxides, but hardly dissolve the dense Ti oxides at low voltage. When the voltage is lower than 1.0 V, the removing of Cu is favourable. The pores or pits form on the sample surface with Cu element dissolved continuously. With increasing voltage, the drive force of removing Cu increases, hence the diameter and depth of nano pores increase. At the same time, the formation of Ti oxides film is enhanced. So the nanoporous structure is only formed on the surface. When the voltage is 1.5 V, the electrochemical polishing becomes favourable. The sample exhibits a relative plat surface. Only shallow pits form due to the local energy fluctuations in the interface between the sample and the solution. The electrochemical polishing means that large quantities of react products would generate; hence, the static current of 1.5 V etching was much higher than that under 1.0 V.
Fig. 1 SEM images of amorphous TiCu alloy after potentiostat etching under (a) 0.5 V; (b) 1 V; (c) 1.5 V

Fig. 2 I-t curves of amorphous TiCu alloy after potentiostat etching under (a) 0.5 V; (b) 1 V; (c) 1.5 V

Fig. 3 shows the microstructure of nanoporous surface prepared by pulse dealloying in 30 wt.% HNO₃ solution for 5400 s. The pulse size is 0.4 V. The insets in the blue square are the low magnification images. Fig. 4 shows the corresponding I-t curves. The Y-axis (I) is mean current density during one pulse interval. The sample subjected to pulse dealloying with 0.5 V initial potential exhibits an inhomogeneous nanoporous surface containing some large holes with diameter of about 100-200 nm and lots of small pits with diameter less than 50 nm, as shown in Fig. 3(a). However, the nano pores exist only on the surface, indicating a single layer nano pores. The pulse dealloying under 1.0 V initial potential results in formation of ideal nanoporous structure with mean pores diameter of about 50-100 nm and mean pore wall thickness of about 50 nm. The nanoporous structure consists of multilayer nano pores. One can observe that inside nano pores exist in the wall or bottom of the surface nano pores, as shown in inset of the Fig. 3(b) (the enhanced image in the red square). The sample subjected to 1.5 V initial potential dealloying exhibits a destructive nanoporous structure (Fig. 3(c)). Low magnification image shows some large pits with diameter of several μm, which consist of destructive nano pores. According to the I-t curves, the static current increases with increasing initial potential. The times to reach static currents for the 0.5, 1.0 and 1.5 V pulse dealloying are about 700 s,
1200 s and 2000 s, respectively. They are shorter than those of potentiostat dealloying, indicating that
the pulse dealloying would favour of formation of nano pores compared with potentiostat dealloying.
The curve (a) in Fig. 4 appears a strange peak in the starting stage. The reason of the peak formation is
not clear and needs to further investigating. Fig. 5 shows the microstructure and corresponding I-t
curve prepared by pulse dealloying in 30 wt.% HNO$_3$ solution for 10800 s. There is no distinct
difference in surface morphology between 5400 s etching (Fig. 3 (b)) and 10800 s etching. The I-t
curve exhibits similar shape, static current and time to reach static current with Fig. 4 (b). The cross
section image shows a multilayer nanoporous structure in the whole ribbon (not shown in the present
paper), indicating that the depth of nanoporous structure would be larger than several µm. However,
only 500 nm nanoporous layer can form on the TiCu ribbon using potentiostat dealloying [21].

The XPS results show that the as-prepared nanoporous sample mainly composes of Ti, Cu and O,
and the contained C (The XPS spectra is not shown here). The proportion of the chemical composition
of Ti to Cu is much higher than nominal atomic ratio of Ti$_{30}$Cu$_{70}$ alloy. The change of proportion of Ti
to Cu between initial alloy and prepared nanoporous structure indicates the reduction of Cu due to the
dealloying process. The Ti2p spectrum is measured as two doublet peaks and one single peak, which
are assigned to Ti$^{2+}$, Ti$^{4+}$ and Ti$^{3+}$, respectively. The single peak in the O1s spectrum is corresponding
to O$^{2-}$. The Cu2p spectrum exhibits a doublet peak which is assigned to Cu$^{+}$. Based on the information
above and analysis of Ti, Cu, and O, the composition of nanoporous structure is TiO, TiO$_2$, Ti$_2$O$_3$ and
small amount of Cu$_2$O.

The formation of nanoporous structure from dealloying started with dissolution of active atoms
on a flat alloy surface, leaving behind vacancies. Before the next layer attacked, the inert atoms diffuse
and start to agglomerate into islands. As a result, the surface is comprised of two distinct kinds of
regions: inert clusters and patches of undealloyed material exposed to electrolyte. However, in the
TiCu binary alloy system, Ti can be self-oxidated to titanium oxides in the HNO$_3$ solution, and then
develop into dense oxide films. In potentiostat manner, the load voltage of 1 V vs SCE is not enough
to break the oxide films consisted of Ti oxides. The potentiodynamic polarization curve of Ti$_{30}$Cu$_{70}$
was examined in 5.36 mol/L HNO$_3$ solution (not shown here). According to the polarization curve, the
breakdown of the passive film occurs at 1.4 V (vs. SCE). It indicates that the oxide film on the surface
is stable under lower applied potential. As a result, further etching would be difficult to carry out. In
the case of pulse dealloying, the oxide film is broken at the pulse peaks since the peaks potential reach
the critical breakdown potential of TiCu alloy. The further etching would occur. After the breakdown
of the oxide film, electrolyte attacks the next layer. As a result, Cu atoms in the next layer dissolve
continually and Ti atoms as well as its oxides agglomerated. When the potential returns to the initial
potential (1.0 V vs. SCE), the oxide film is self-recovery and the over-corrupt is avoided. Ultimately,
this periodic process leads to the formation of multilayered nanoporous structure.
4. **Conclusions**

We prepared nanoporous Ti oxides by potentiostat and pulse dealloying TiCu amorphous alloy. Three events would be suggested for potentiostat dealloying TiCu alloy in HNO₃ solution: removing the Cu element, forming oxides film and electrochemical polishing. Multilayer nanoporous structure was fabricated using pulse dealloying. The pulse dealloying under 1.0 V initial potential results in formation of an ideal nanoporous structure with mean pore diameter of about 50-100 nm and mean pore wall thickness of about 50 nm. The static currents for pulse dealloying are higher than those for potentiostat dealloying under the same initial potentials.

Acknowledgments: This work was supported by National Natural Science Foundation of China (50901051) and Key Projects in the Tianjin Science & Technology Pillar Program (09ZCKFGX29100).
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