



Regular article

Ultrastable metal oxide nanotube arrays achieved by entropy-stabilization engineering

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ARTICLE INFO

Article history:

Received 11 October 2017

Accepted 15 December 2017

Available online xxxx

Keywords:

Entropy-stabilization engineering

High-entropy alloys

Anodization

Multicomponent oxide nanotubes

Thermal stability

ABSTRACT

Metal oxide nanotube arrays have recently attracted extensive attention due to their widespread use in the field of catalysis and energy storage. However, the low structural stability of the currently available nanotube arrays severely limits their efficiency and high-temperature applications. By applying the entropy-stabilization engineering strategy, we developed ultrastable metal oxide nanotube arrays consisting of multiple oxide constituents by anodic oxidation of high-entropy alloy precursors, which can sustain 800 °C heat-treatment without crystallization and resist 1000 °C calcination without collapse. The superior thermal stability endows the high-entropy oxide nanotube arrays a promising candidate for high-temperature applications.

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In the past, searching for advanced materials with enhanced properties to meet urgent industry demands was primarily based on enthalpies of formation. Recently, entropic contributions to the free energy were taken into account for alloy design by the metallic materials community, and configuration disorder was compositionally engineered into one single crystallographic lattice by deliberately selecting five or more constituents to minimize effects from cohesive energy [1–3]. In these “high-entropy” alloys (HEAs), entropic contribution to the free energy predominates the thermodynamic landscape, particularly at elevated temperatures [4]. As a result, such entropy-stabilized alloys which possess a single-phase structure usually show a heavily suppressed atomic diffusion and ultrahigh thermal stability against temperature. More recently, Rost et al. extended the entropy-stabilization concept to non-metallic systems and successfully developed five-component mixed oxides with a single-phase solid solution structure [5]. With the increase of the configuration disorder, the solid-state transformation from multiple phases to the single-phase rock salt was effectively promoted, resulting in a significant reduction in the conversion temperature.

Nanoscale metal oxides such as nanotubes and nanopores, have been extensively investigated [6,7] and widely used in a variety of advanced technologies such as dye-sensitized solar cells [8–10], gas sensors [11,12], and catalysis [13,14]. Although substantial advances have been made in this area, synthesis of metal-oxide nanostructures with superior structural stability remains to be a major challenge [15–19]. For example, anodic amorphous nanotube arrays usually crystallize at 300–500 °C, and the entire nanotube architecture collapses

below 800 °C. Such low structural and morphological stability severely restrict their engineering applications especially at elevated temperatures.

Inspired by both the work of “entropy-stabilized oxides” and the research activities of HEAs, we aim to develop single-phase nanotubes consisting of multicomponent mixed metal oxides which are expected to be highly stable at elevated temperatures based on thermodynamic considerations. In this paper, we report synthesis of a new class of entropy-stabilized, multicomponent oxide nanotube arrays with a monolithic amorphous phase at room temperature. The as-prepared amorphous nanotube arrays can sustain 800 °C heat-treatment without crystallization and resist 1000 °C calcination without collapse. The superior thermal stability endows the high-entropy oxide nanotube arrays a promising candidate for high-temperature applications with much enhanced efficiency.

Alloy ingot with a nominal composition of TaNbHfZrTi HEA was prepared by arc-melting in a Ti-gettered high-purity argon atmosphere. The sample was then solutionized at 1400 °C for 24 h in Ar gas atmosphere, followed by water quenching. A two-electrode system with a platinum gauze as a counter electrode was used for electrochemical experiments. The electrolyte used was 1 M (NH₄)₂SO₄ with 0.5 wt% NH₄F. Anodic oxidation was performed at ambient temperature with an anodization potential of 70 V for 4 h using a high-voltage potentiostat (IT6514E). After the anodization, the oxidized samples were abundantly rinsed in deionized water followed by drying in N₂ stream. Annealing of the samples was carried out in air at different temperatures (800, 900 and 1000 °C) for 1 h with a heating rate of 4 °C/min in an electronic furnace (SG2-3-12), followed by cooling with furnace. The morphology and microstructure of the nanotubes was analyzed by Zeiss Supra™ 55 field emission scanning electron microscope (FE-SEM) and Scanning

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Transmission Electron Microscopy with Energy Dispersive X-ray Spectroscopy (STEM-EDS) (FEI Titan G2 60–300 ChemiSTEM, 300 kV). The composition and the chemical state were characterized by using X-ray photoelectron spectroscopy (XPS, PHI Quantera SXMTM, Mg K α). Crystallization behavior of the as-grown nanotubes was examined by differential scanning calorimetry (DSC) in a Netzsch STA449C apparatus at a heating rate of 5 °C/min.

The reason for selecting the TaNbHfZrTi HEA as the precursor for anodic oxidation is twofold; one is that the equiatomic TaNbHfZrTi alloy, a typical HEA with a single body-centered cubic (BCC) crystal structure, has been studied extensively due to its excellent mechanical properties [20–22]. The other is that each constituent in the HEA, i.e., Ta, Nb, Hf, Zr and Ti, has already been utilized to grow oxide nanotube layers [6]. Therefore, it is highly possible to obtain self-assembled multicomponent metal oxide nanotube arrays by anodic oxidation of this representative HEA.

The morphology and structure of the as-grown oxide nanotubes are shown in Fig. 1. Clearly, highly ordered arrays consisting of densely packed nanotubes with an open top and a closed bottom were obtained. From Fig. 1a–d, it is seen that the thickness of the as-grown nanotube layer and the diameter of the tubes are approximately 17 μm and 240 nm, respectively. Fig. 1e shows TEM images of several typical nanotubes. The nanotube wall thickness was determined to be 33 ± 4 nm. The inset in Fig. 1e illustrates a selected area electron diffraction pattern (SAED) of the as-grown nanotubes, indicating a typical amorphous structure. Fig. 1f depicts STEM-EDS measurements of the as-grown nanotubes. Apparently, all constituents are homogeneously distributed in the sample.

We therefore refer to the self-assembled multicomponent oxide nanotubes as high-entropy oxide network, which is, to the best of our knowledge, the first such example for metal oxide nanotubes.

Fig. 2a–e display the high-temperature calcined nanotubes arrays and their corresponding TEM images. The tubular architecture of all the samples is well preserved after calcination at each temperature, and no discernible changes in the layer length and tube size were observed (Fig. 2a–c). The architecture stability of our anodic oxide nanotube arrays is the highest ever reported in self-organized anodic oxide nanotubes [23–35]. SAED patterns of 15 local locations in the nanotubes annealed at 800 °C were obtained. As an example, Fig. 2d shows three of them marked as A, B and C in a tube, which ambitiously reveals that the nanotubes still remain the amorphous state after being annealed at 800 °C.

Fig. 2e shows microstructure of the nanotubes annealed at 900 °C. Obviously, crystallization of the amorphous nanotubes occurred and small grains can be clearly observed, indicating that the amorphous-crystalline transformation of the as-grown nanotubes starts near 900 °C. Full nanocrystallization was also observed in the nanotubes annealed at 1000 °C for 1 h. The diffraction spots in the SAED patterns indicate that the annealed oxide nanotubes contain multiple phases (the inset in Fig. 2e). Further STEM-EDS measurements clearly indicate that there are (Ta, Nb)-rich phases (Phase I in Fig. 2f) and (Hf, Zr, Ti)-rich phases (Phase II in Fig. 2f) in a nanotube annealed at 1000 °C. In other words, the as-grown high-entropy amorphous metal oxide nanotube arrays crystallized into multiple oxide compounds, rather than a single solid-solution phase.

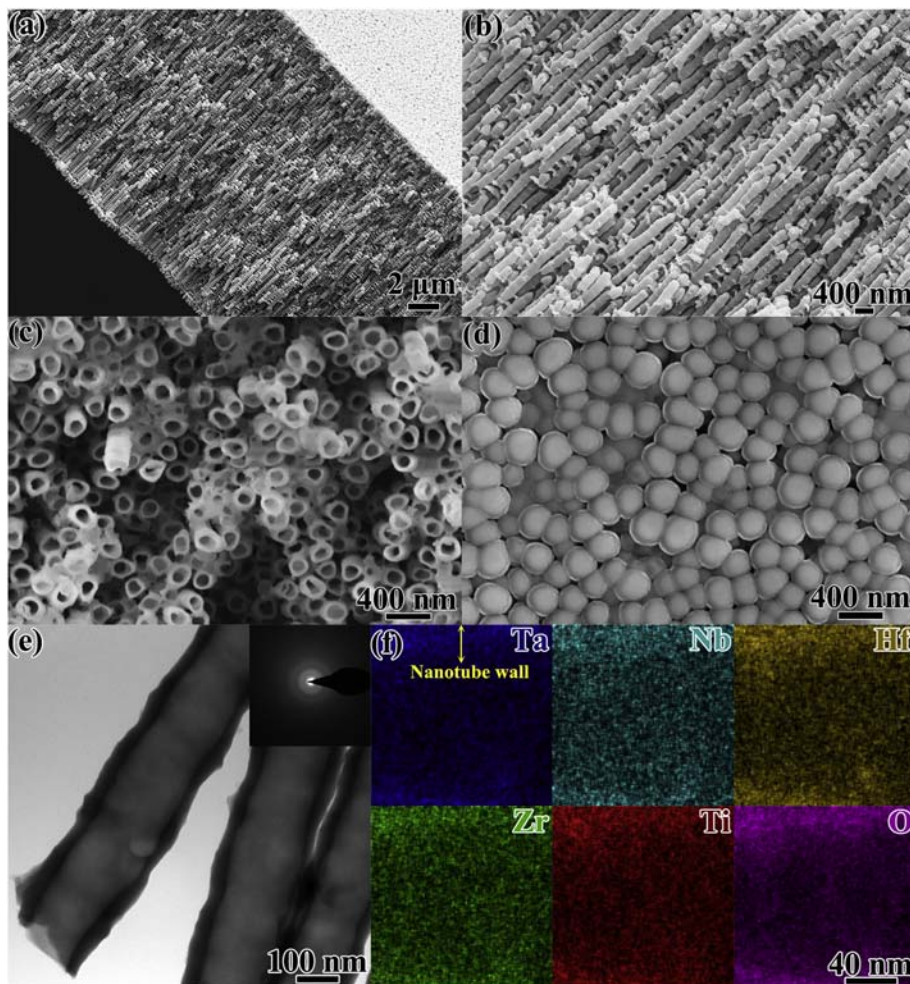


Fig. 1. (a) FE-SEM cross-sectional, (b) its enlarged view, (c) top-view and (d) bottom-view images of the as-grown multicomponent oxide nanotubes, and (e) the corresponding TEM and (f) STEM-EDS images.

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