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Phase dependent magnetic properties of Ni–Au alloy nanowires

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ABSTRACT

Binary alloy nanowires of mutually immiscible Ni–Au system are synthesized by electrodeposition method. Here, we incorporate the concept of alloy design into nanowires to effectively engineer and control the magnetic properties of nanowires. Saturation magnetization and coercivity values of as-deposited Ni–Au alloy nanowires strongly correlate with either the phases present or to the dissolution of gold to nickel. The magnetic properties, however, were significantly affected upon annealing, which is correlated with the structural evolution of a weakly magnetic metastable *hcp*-Ni phase. We report here the detailed investigation on phase transformations in Ni–Au alloy nanowires and their effect on magnetic properties.

1. Introduction

Recently, one-dimensional nanostructures, particularly nanowires, have stimulated extensive research interest for magnetic applications. Single component or multilayer barcode metallic nanowires with Ni, Co and Fe have been explored to optimize the magnetic properties [1–6]. However, controlling the diameter or thickness of the single or barcode nanowires to modify the magnetic properties is not always possible due to limitations in choosing the nanowire diameter for real-world applications.

In this study, beyond basic scaling approaches such as size reduction, the concept of nano-alloying (compositional modification of nano-structures) has been exploited in nano-material design to modulate magnetic properties of nanowires. We have modified the microstructure of Ni-nanowires by alloying them with Au. Using the facile electroplating method, we fabricated Ni–Au alloy nanowires with metastable structures at room temperature. Starting from a very fine nanocrystalline metastable structure, a subsequent heat treatment resulted in phase evolution of the hexagonal close packed (*hcp*) Ni phase, which is an unconventional metastable structure for Ni. These metastable Ni–Au nanowires exhibit significant differences in their magnetic properties compared with that of typical Ni nanowires. Our new findings not only deepen our fundamental understanding of metastable phase formation from nano-alloying but also open the door to modulating magnetic properties of transition-metal nanowires by controlling the intensity of ferromagnetism for future magnetic applications.

2. Experimental

In the present investigation, Ni–Au alloy nanowires were fabricated using an electrodeposition on Anodisc 25 anodic aluminum oxide (AAO) templates from Whatman. Ni–Au alloy nanowires were electrodeposited from an electrolyte comprising nickel sulfate ($NiSO_4 \cdot 6H_2O$, 0.5 M), boric acid (H_3BO_3, 0.2 M) and potassium gold cyanide ($KAu(CN)_2$, 0.005 M). The electrodeposition was performed at a pH of approximately 3 and a current density of 5 mA cm^{-2}. Details of electrodeposition experiments for the synthesis of nanowires using AAO templates can be found elsewhere [7]. The composition of Ni–Au nanowires were approximately 68 at% Ni and 32 at% Au as confirmed by inductively coupled plasma (ICP) spectroscopy and energy-dispersive x-ray spectroscopy (EDS) analysis. Annealing of the Ni–Au alloy nanowires was performed together with the AAO template in an inert argon atmosphere for 1 h at 473 K. As a reference, pure Ni nanowires were also electrodeposited from an electrolyte composed of nickel sulfate ($NiSO_4 \cdot 6H_2O$ 0.5 M) and boric acid (H_3BO_3, 0.2 M). A current density of 5 mA and pH of approximately 3.5 was maintained in the electrolyte during electrodeposition. Both pure Ni and Ni–Au alloy nanowires were characterized by transmission electron microscopy (TEM) for microstructural characterization using either a CM 30 (Philips) or JEM-3010 (JEOL). From the bright field image (Figs. 1 and 2a), it is clear that the diameter of the nanowire is approximately 200 nm. Crystal structure determination of nanowires was performed by both x-ray diffraction (XRD) and selected area electron diffraction (SAED)

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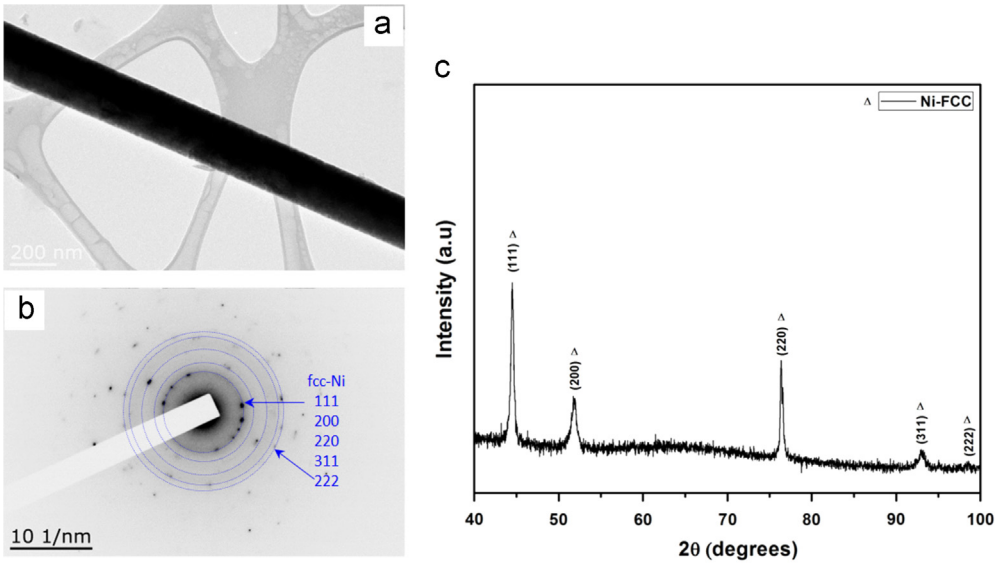

Fig. 1. XRD and TEM analyses of Ni nanowires (a) bright field image showing Ni nanowire, (b) corresponding SAED pattern, and (c) XRD pattern for Ni nanowires in the as electrodeposited condition.

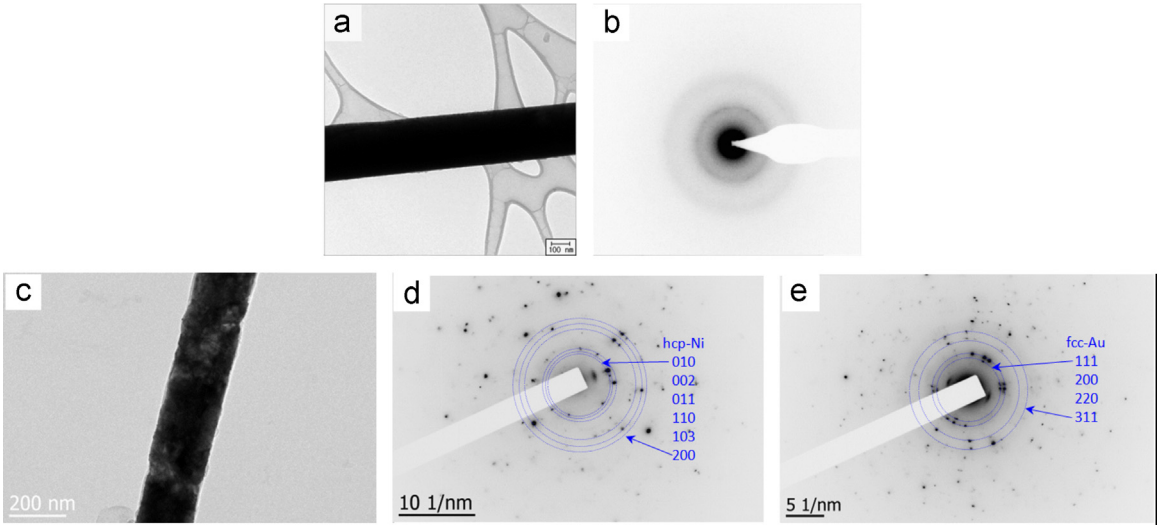

Fig. 2. TEM micrographs of as electrodeposited Ni–Au alloy nanowires (a) bright field image showing nanowire, (b) SAED pattern taken shows very fine nanocrystalline nature of the nanowire, (c) bright field image showing Ni–Au alloy nanowire annealed at 473 K for 1 h, (d) and (e) SAED patterns taken from 2 different regions of the nanowire indexed to *hcp*-Ni and *fcc* Au crystal structures.

patterns of TEM. Moreover, in-situ phase transformation studies were conducted on the Ni–Au alloy nanowires to study phase evolution over a range of temperatures using a high temperature XRD (PANalytical X'pert prohtk 1200N) under an inert atmosphere. Magnetic measurements were performed on a Vibrating sample magnetometer (VSM) (MicroSence, EV9) to determine the saturation magnetization M_s and coercivity H_c of the Ni and Ni–Au alloy nanowire arrays embedded in the AAO templates.

3. Results and discussion

Fig. 1a and b show the bright field image and the corresponding SAED patterns of the electrodeposited Ni nanowires, respectively, which have been indexed to face centered cubic (fcc) crystal structure as expected. In addition, the XRD patterns of the pure Ni nanowire sample after electrodeposition are shown in Fig. 1c. From the Bragg peaks of the x-ray diffractogram, one can index and confirm the Ni fcc crystal structure.

By contrast, the Ni–Au nanowires had quite different microstructures. TEM analysis on the electrodeposited Ni–Au alloy nanowires is shown in Fig. 2. The bright field image and SAED pattern are shown in Fig. 2a and b, respectively. The selected area electron diffraction pattern shows the diffused rings, which could indicate either a very fine nano-crystalline or amorphous phase. The TEM analysis of the Ni–Au electrodeposited alloy nanowire after annealing at 473 K for 1 h is shown in Fig. 2c–e. The bright field image of the annealed Ni–Au alloy nanowire at 473 K is shown in Fig. 2c, while and the corresponding SAED pattern indexed to *hcp*-Ni phase, is shown in Fig. 2d. Similarly, the SAED pattern of the annealed Ni–Au alloy nanowire from a different region is shown in Fig. 2e indexed to fcc Au crystal structure. Thus, upon annealing, we speculate that an initial metastable nanocrystalline Ni–Au phase has been evolved into a nanocomposite or nanohybrid structure composed of both *hcp*-Ni, and fcc-Au.