

Novel Method for the Electrochemical Synthesis of Nickel-Rich Oxide Nanowires

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ABSTRACT

Using a novel electrochemical process, functionalized and self-assembled Ni-rich oxide nanowires were grown from an Alloy 600 (Ni – 15.5a/o Cr, 8a/o Fe) substrate. The formation of the nanowires occurs in a high-temperature (238-288°C), high-pressure (1500psi) aqueous solution by subjecting Alloy 600 to a specific progression of reducing and oxidizing conditions. The nanowires have an average diameter of 25nm with a range from 3nm to 100nm with a maximum observed length of 20µm. Energy dispersive spectra of individual nanowires have indicated a composition of 47a/o Ni, 4a/o Fe, 49a/o O. Their composition, in conjunction with the oxidizing growth environment, suggests that the nanowires are corrosion resistant, an important property for biotechnology applications. SQUID magnetometry shows the nanowires to be ferromagnetic, with a coercivity of approximately 80Oe and a remnant field of 0.027emu/g.

1 BACKGROUND

In recent years, the field of nano-systems, and in particular nanowires, has received much attention for its potential application ranging from arrays of sensors for detection of particular biological agents [1-3] to the building blocks for logic circuits [4-5]. However, the progression of the field has been retarded by the limited number of synthesis techniques and subsequent lack of control of material properties needed to functionalize the nanowires. Thus, any novel nanowire synthesis process that can produce new chemical compositions of nanowires with functional properties represents a step forward for the field.

We have discovered a novel electrochemical method for the synthesis of nickel-rich oxide nanowires formed by self-assembly. The advantage of self-assembly is that growth occurs directly on the substrate, without the use of a template or catalyst [6-9] (which requires later processing steps to remove). Preliminary analysis has shown the nanowires to already have a desirable set of functionalizable properties including electrical conductivity (as demonstrated by their appearance in electron microscopes) and ferromagnetism. Additionally, because many metal oxides have low

solubilities over a wide range of pH [10], our nanowires should be viable for application in aqueous solutions, especially in highly oxidizing environments, such as the conditions found in the human body.

2 EXPERIMENTAL METHOD

Synthesis takes place in an autoclave designed to simulate the conditions found inside of a pressurized water reactor (PWR) of a nuclear power plant. The autoclave and attached piping are constructed out of titanium to prevent corrosion, and are built to withstand operating temperatures of 288°C and pressures of 1500psi (necessary to prevent the aqueous solution from boiling off at operating temperatures). The inner chamber, (shown in Figure 1) where the samples are held, is approximately 50cc and has interlocks for a thermocouple, two Cu/CuO reference electrodes, and for wires connected to the sample.

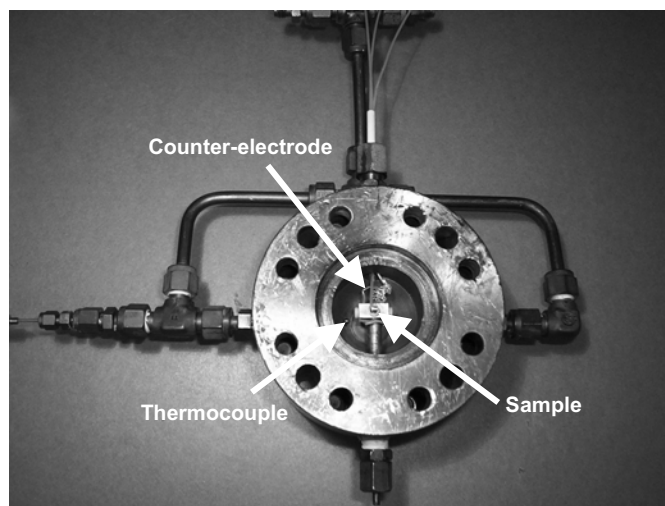


Figure 1: Open autoclave with mounted sample.

Each substrate is prepared using the same procedure. Using a low-speed saw, samples are cut into approximately 1/8 x 1/8 x 3/8 inch pieces, which is the maximum size than can be accommodated by the autoclave sample holder. The samples are then notched using a file, such that a Teflon[®] pin holds the sample in place in the autoclave's sample carrier.

Each substrate is then polished using a progression of finer grit polishing paper, concluding with 600 grit SiC, in order to remove any thick layer of surface oxide. The samples are then cleaned in a sonication bath using twice deionized water. Finally using a spot welder, a Teflon[®]-sleeve protected stainless steel wire is attached so that electrical connection can be made to the sample and the substrate is mounted in the sample carrier of the autoclave. Two samples of the same type can be mounted and simultaneously tested for each trial.

Once the samples are mounted, the chamber is sealed. Gold is used for the body and window seals and Teflon[®] for the wire seals to prevent the possibility of contamination due to the oxidation of other species during the experimental process. The chamber is connected to the pump and heating system and filled with an aqueous solution composed of deionized water containing 2ppm Li and 1200ppm B. The normal flow rate of the system is approximately 50cc/min, such that the experimental chamber is refilled with fresh solution once a minute. Both samples, the gold counter electrode, and the Cu/CuO reference electrode are connected to a Solartron SI 1287 potentiostat. The autoclave is heated to 288°C and concurrently pressured to 1500psi to prevent the solution from boiling. The potentiostat is activated after the autoclave has exceeded 170°C because the electrical conductivity of the Zirconia tube that houses the Cu/CuO is too low at temperatures below this value.

The samples are then taken through a polarization progression which can be broken into 3 basic polarization categories. The first step is cathodic polarization (-1600mV with respect to the standard hydrogen electrode, SHE), to reduce any oxide films formed with exposure to the air before the experiment or during the course of the heating of the water. Second, the substrate is polarized to -850mV in order to grow a Cr₂O₃ film, whose identity has been verified by previous surface enhanced Raman spectroscopy (SERS) studies [11]. Finally, the sample is polarized between -250mV to -25mV vs. SHE, where it has been shown that nanowire growth occurs.

Analysis of each substrate begins with an examination of the surface with a field-emission scanning electron microscope (FESEM) in order to determine the area, extent, and morphology of nanowire growth. Once this is catalogued, one of the two samples is immersed in an isopropyl-alcohol (IPA) bath and sonicated, effectively shaking wires off the surface of the sample into the solution. A drop of that solution is placed on a holey carbon transmission electron microscope (TEM) grid and the IPA is allowed to evaporate, leaving the nanowires (and whatever other oxides that were also stripped off in the process). Diffraction analysis is performed using a JEOL 200CX and compositional analysis is performed using electron dispersive spectroscopy (EDS) and verified using electron energy loss spectroscopy (EELS) on a Philips CM-200.

Samples for magnetic analysis are prepared by first selecting an area of the sample completely covered by nanowires (as shown by FESEM). Once a suitable area is identified, the nanowires are torn off the surface using a piece

of household Scotch[®] tape. The mass of the nanowires removed is determined by measuring the weight of the tape before and after the nanowires are applied. The substrate is subsequently examined on the FESEM to verify that only a portion of the nanowire layer was removed (i.e. other surface oxide layers were not torn off as well). The tape is then placed in an inert gel capsule and inserted into a SQUID magnetometer where two magnetic tests are performed. The first examines the hysteresis of the nanowires by measuring magnetization as a function of applied field for a given temperature, in order to determine remnant field and coercivity. Second, magnetization is measured with changing temperature in order to determine if the Curie temperature of the nanowires lies within the temperature range of the magnetometer.

3 RESULTS / DISCUSSION

3.1 Processing

Approximately 15 tests with various values of process parameters have been conducted in which nanowires have been successfully synthesized.

The first parameter to be investigated is the role of substrate. Nanowires (shown in Figure 2) were first discovered on Alloy 600 (Ni – 15.5a/o Cr, 8a/o Fe), while conducting stress corrosion cracking investigations of the alloy. The majority of subsequent tests have also been conducted on this alloy however a variety of other samples have also been tested using the same processing parameters that produced nanowires on Alloy 600. Nanowires were grown on a Ni – 30a/o Cr binary alloy (Figure 3a) as well as a Ni – 20a/o Cr – 10a/o Mo ternary (Figure 3b), while pure Cr produced nanoparticles (aspect ratio about 4:1), and Ni and Fe did not produce nanowires.

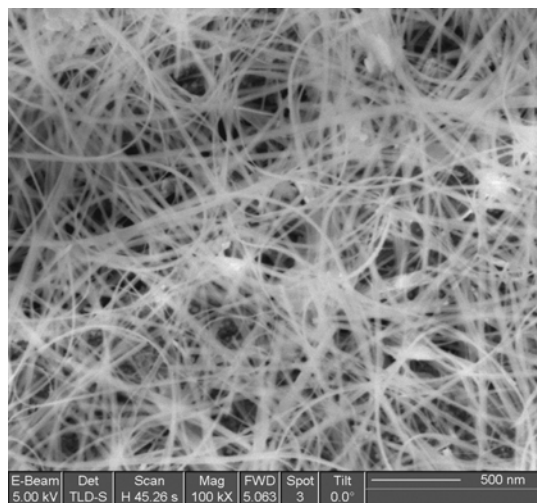


Figure 2: Nanowires grown on Alloy 600 at 288°C. Substrate held at -1600mV for 24 hours, -850mV for 1 hour, and -25mV for 40 hours.

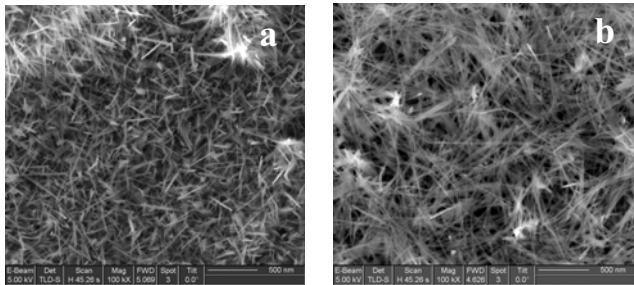


Figure 3: Nanowires grown on (a) Ni – 30a/o Cr binary alloy and (b) Ni – 20a/o Cr – 10a/o Mo ternary using same hydrogen- oxygen cycling.

The next major processing parameter found to be of importance to the synthesis process is the composition of the aqueous solution. Alloy 600 anodically polarized in an aqueous solution of deionized, deoxygenated water, with 2ppm Li, and 1200ppm B grew nanowires while the same test conducted in deionized, deoxygenated water without any Li and B did not. An important difference between the two cases is the pH of the solution at 288°C. With the electrolyte, the calculated pH is 6.75 [12], while the pH of pure water is 5.5 at 288°C. If the edge of the thermodynamic stability of the nanowires lies somewhere in between these two values, this would explain the observation.

Finally, growth of nanowires was found to be highly dependent on the potentials applied and the duration of the applications. Tests have shown that it is necessary to first bring the substrate to a reducing potential (in-situ surface enhanced Raman spectrometry has shown -1600mV to be very effective at this), perhaps to reduce any surface oxides that may be residing on the surface to clear a way for the nucleation of the nanowires. It may also be the case that in order for nanowires to grow, a Cr₂O₃ layer needs to be grown first, which has been found to form at -850mV [13]. Finally, tests show that potentials above -250mV need to be applied for the growth of nanowires. Typically, -25mV is utilized because these tests produce full surface coverage of nanowires, but potentials above -25mV have not been attempted yet. We have also shown that reducing potentials need to be applied for as little as an hour and other tests have shown that nanowire nucleation begins in less than 30 minutes of -25mV being applied (see Figure 4). However, for complete surface coverage, -25mV needs to be applied for over 4 hours (most tests usually lasted about 2 days at this potential).

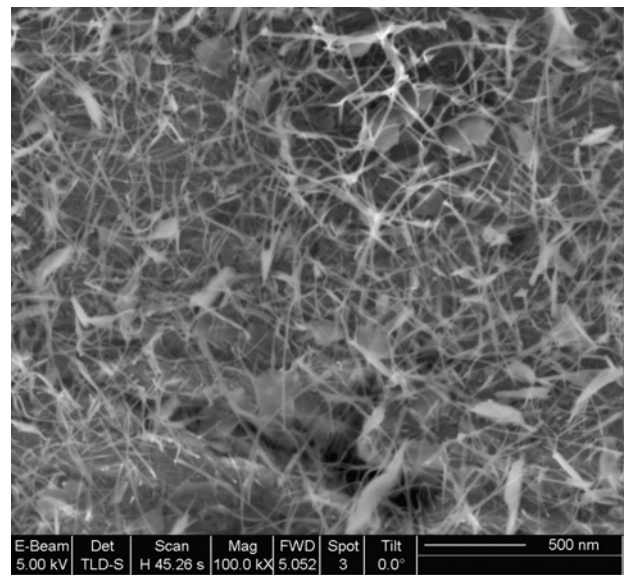


Figure 4: Nanowires beginning to form after being held at -1600mV for 24 hours, -850 mV for 1 hour, and -25mV for 30 minutes.

3.2 Properties

Scanning electron micrographs reveal nanowires as long as 20 microns with uniform thicknesses along the length of single nanowires, although a distribution of thicknesses exists between different wires. TEM analysis of over 300 wires shows the average diameter of the wires to be 25nm, with a standard deviation of 17nm. The maximum thickness was 90nm with the majority of the wires between 20-30nm. The nanowires have aspect ratios of 100:1 to 1000:1.

EDS analysis conducted on a TEM (and verified by EELS) shows the wires grown on Alloy 600 to be 47a/o Ni, 4a/o Fe, 49a/o O. This coupled with diffraction analysis suggests a crystal structure very similar to bulk NiO, however, it is unclear whether the role of Fe is substitutional or if it exists as a separate phase. Diffraction does show the nanowires to be single crystalline.

SQUID magnetometry indicates the nanowires grown on Alloy 600 are ferromagnetic as shown by the hysteresis loop in Figure 5. At 5K, the nanowires produce hysteretic loops with coercive fields of 150Oe and remanence of 0.039emu/g. Magnetization as function of temperature with an applied field of 250Oe shows that the Curie temperature lies above 400K (the temperature limit of the magnetometer).

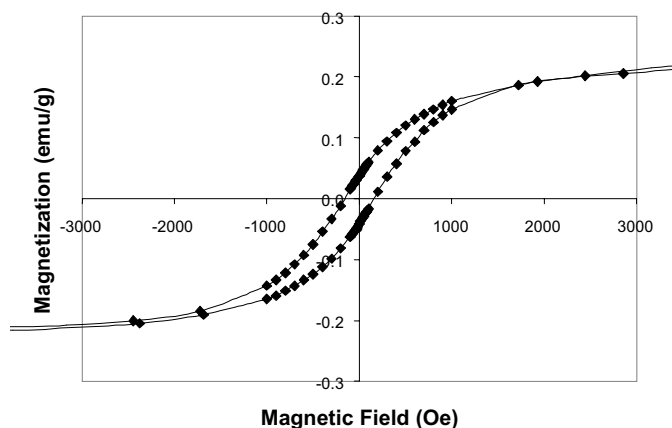


Figure 5: Magnetization versus applied field at 5K for a 0.3mg sample of nanowires grown from Alloy 600.

4 CONCLUSION

We have demonstrated that self-assembled nickel-rich oxide nanowires can be grown using a novel electrochemical process on a variety of nickel-based alloys. Nanowires grown on Alloy 600 have an average diameter of around 25nm and aspect ratios up to 1:1000, a composition of 47a/o Ni, 4a/o Fe, 49a/o O, and ferromagnetic behavior under applied magnetic fields. Future research will be focused on identifying and understanding the mechanism of growth as well as determining electrical, optical, and structural properties.

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