



Radially arrayed nanopillar formation on metallic stent wire surface via radio-frequency plasma

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ABSTRACT

MP35N (Co–Ni–Cr–Mo alloy) is an important stent implant material for which many aspects, that include nanostructured surfaces, are yet to be understood. The present study provides the first creation of radially emanating metallic nanopillar structures on the surface of MP35N stent alloy wires; a novel textured surface structuring derived via controlled RF processing technique. The goal of this study was to characterize the newly found structures, identify evolution stages of nanopillar formations, as well as optimize RF process parameters for controlled surface texturing technique for stent wire materials. The exposure of a stent alloy wire, 250 μm diameter Co–Ni–Cr–Mo alloy (MP35N), to parameter-controlled RF environment resulted in dense surface nanostructures consisting of high-aspect-ratio dendritic nanopillars/nanowires. Extensive surface characterization and local compositional analyses by Transmission Electron Microscopy (TEM), Energy Dispersive X-ray analysis (EDX) and X-ray photoelectron spectroscopy (XPS) show increased values of Mo contents on the outer edges of protruding nanopillars, indicating a possibility of the higher Mo content phase contributing to the differential plasma sputter etching on the MP35N surface and resultant nanowire formation. A comparative investigation on single phase alloy versus multiphase alloy seems to point to the importance of phase segregation for successful nanowire formation by RF plasma treatment. In addition to MP35N, some specific single phased materials, such as Fe–Ni and Fe–Cr alloys or Pt metal wire, were exposed in same RF plasma conditions and results did not form the complex structures found on MP35N samples. For the purpose of this study, metallic stent wires that have nanostructured surfaces can be considered a “polymer-less” approach to surface modification. The creation and characterization of radially arrayed nanostructured surfaces has been demonstrated on MP35N stent alloy wires using this RF plasma process; where such nanostructured surfaces contribute to design concepts that may enhance endothelialization of stent materials via surface texturing modification.

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1. Introduction

Cardiovascular disease is known to be the number one cause of death and disability in the United States and most European countries. The use of metallic stents such as a Co–Cr–Ni–Mo alloy (often called MP35N), especially in the drug-eluting stents (DES) has contributed greatly to reducing the scope of such cardiovascular problems [1,2]. However, research data suggests that the polymer material utilized in the DES designed for drug release may induce undesirable thrombosis [3]. Indeed, data outside of clinical trials show higher drug-eluting stent thrombosis rates than observed in clinical trials or with bare metal devices [4], making bare metallic stents or all metallic stents an attractive option. Nanotextured coatings fit into a category of design concepts that enhances endo-

thelialization of stent struts and may reduce late thrombosis [5]. Specifically, vascular smooth muscle and endothelial cell densities were improved on PLGA films that possess increased nanometer surface roughness without changes in chemistry [6]; where improved endothelial cell densities as a result of increased surface roughness is emphasized. For the purpose of this study here, metallic stent wires that have nanostructured surfaces can be considered a “polymer-less” approach to surface modification, where fully metallic metal wires with a dense forest of surface nanostructures can be considered as an alternative option for efforts to improve stent material design.

While there have been many recent publications on nanowire formation of carbon nanotubes, ZnO, Si, GaAs, and so forth, e.g., by high-temperature chemical vapor deposition, little research has been reported on fully metallic nanowire formation involving rapid high-temperature processing. In this paper, the creation of fully metallic nanowires radially protruding from surfaces of

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medical grade alloy wires via RF plasma processing is presented. Motivation behind this research lies in optimizing the nanowire formation, understanding the principles involved in the RF plasma surface texturing process, and characterization of resulting surface nanostructures.

2. Materials and methods

The sample alloy wires used for experiments are made of medical grade alloy MP35N (35% Co–35% Ni–20% Cr–10% Mo in wt.%) having a 250 μm diameter and electropolished smooth surface. This 250 μm dimension is comparable to a strut diameter of some of the medical stents. For texturing, five of approximately 10 cm long wire samples were mounted vertically at the cathode plate base at 2.5 cm spaced apart from the neighboring wires as demonstrated in Fig. 1. Within this wire mounted region, the RF plasma texturing results were identical, independent of the location of sample mounting in chamber. Experiments were performed using a custom-built RF plasma system, with the RF powered cathode using 30 sccm of Ar gas with a base operating pressure around 2.0×10^{-2} Torr and 100–200 W power. The temperature rise of the MP35N wire samples was monitored using visual inspection and IR thermometer, and was estimated to be in the 800–1000 $^{\circ}\text{C}$ range. After RF plasma processing, surface microstructures of the MP35N wire samples were investigated by scanning electron microscope (SEM), transmission electron microscope (TEM), Electron Back Scattered Diffraction (EBSD) analysis.

3. Results and discussion

3.1. RF plasma processing for surface nanostructure

Our methodology of RF processing has led to a number of unexpected observations of unique surface morphologies on the MP35N wires [3]. It is believed that ion bombardment was a key to creating nanowire morphologies that vary in shape with various RF process parameters [7]. It is of interest to understand our RF process control on modifying topography of MP35N wire surfaces. Recent in vitro research findings suggest that biomaterials with nanoscale surface topography can influence cell behavior like adhesion, proliferation, and differentiation [8], where surface texturing on implantable medical device materials may improve cellular attachment in biomedical applications [9]. The common alloys for coronary stents available on the market today are MP35N, L605 CoCr and stainless steel grade 316L [10]. The current study reported here focuses on MP35N alloy and the unique variation of resulting metallic nanowires and nanostructures on the surface after RF processing surface modification. Although the focus on this research

does not entail cell experimental data, future research to help identify whether or not our textured MP35N surface will support cell proliferation and adhesion is an attractive strategy worth investigation once we have more understanding of RF processing and control for texturing MP35N stent wires.

The multi-phase alloy, MP35N (35 wt.% Co–35 wt.% Ni–20 wt.% Cr–10 wt.% Mo), was developed in the 1960's and is primarily used in orthopedic implants. Due to its high strength, this material is currently used as the lead wire for pacemakers, and as a substitute for 316L stainless steel in cardiovascular stents [11]. MP35N is a cobalt–nickel based superalloy sometimes used for low to moderate temperature applications requiring high strength, high toughness, and high corrosion resistance. When fully annealed at temperatures above 850 $^{\circ}\text{C}$ (a full anneal of MP35N in a few minutes will occur at 1010–1177 $^{\circ}\text{C}$) [12], MP35N is a single phase solid solution with a face-centered-cubic (fcc) structure [13,14]. The strain induced martensite phase (martensitic hexagonal-close-pack) is believed to be formed during room temperature deformation. However, there is little understanding of the microstructural origin of the secondary hardening, and a detailed characterization of the secondary hardening phenomenon is also lacking [15].

MP35N wire samples exhibit a multi-phase structure containing fcc and hcp phases. High-temperature exposure of the MP35N material such as by aging heat treatment enhances the formation of stacking faults and Mo segregation [15]. In fact, in our RF plasma processed MP35N wires, we have observed generally higher Mo concentration on the outer surface of the nanowire/nanopillar MP35N wire samples. Our preliminary EDS analysis indicates that the surface area including nanowire/nanopillar regions tend to have higher Mo contents than the interior regions. However, it is not clear if this 100 nm scale segregation behavior is related to Asgari et al.'s observation of nanoscale, stacking-fault-based phase segregation. Rather, it is speculated at the moment that the significantly different sputter rate of Ni and Co (by a factor of ~ 2) compared to that of Mo is likely to lead to continuously varying alloy composition on the MP35N wire surface as the sputter etching proceeds under RF plasma condition applied (and hence continuously altered, local phase diagram moving toward two-phase or multi-phase regime). This will be discussed in the later section. Further research is needed to fully understand the underlying mechanisms of phase segregation in RF processed wire materials. It is important to note that the RF process, as compared to DC plasma process, advantageously creates the necessary high-temperature condition in the sample to induce the nanowire formations, in addition to the ion bombardment effect which also contributes to the temperature rise. In general, plasma etch processes have low-energy ions that release their energy just below the surface of the solids which may result in the removal of the surface atoms [7]. As a result of such sputtering, ripple-like structures can appear on the surface

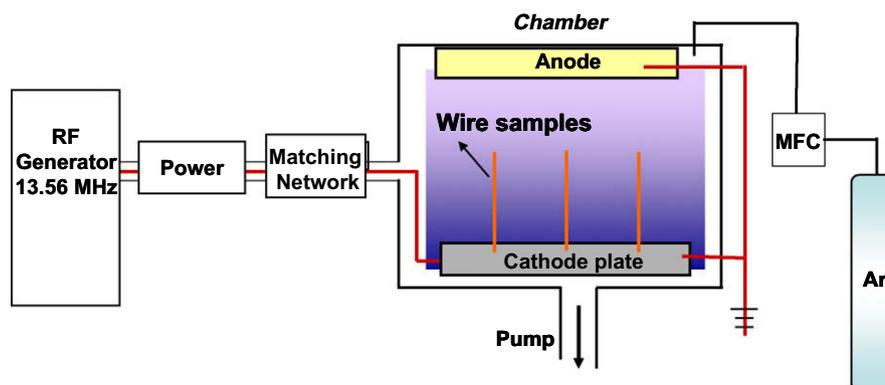


Fig. 1. Schematic shown is an illustration of RF plasma processing of MP35N alloy wires.

ID	Title	Pages
2548	Radially arrayed nanopillar formation on metallic stent wire surface via radio-frequency plasma	7

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