Evidence of metastable hcp phase grains in as-deposited nanocrystalline nickel films

S. Rajasekhara, K.J. Ganesh, K. Hattar, J.A. Knapp and P.J. Ferreira

Sandia National Laboratories, Albuquerque, NM 87185, USA
Materials Science and Engineering Program, The University of Texas – Austin, Austin, TX 78712, USA

Received 14 February 2012; revised 12 April 2012; accepted 16 April 2012
Available online 20 April 2012

Precession microscopy is applied to determine the morphology of pulsed laser deposited and unannealed Ni films. The nanostructure of these films, nominally 50 nm in thickness, is heterogeneous and comprised predominantly of face-centered cubic (fcc)-Ni phase with regions of \( \{101\}_\text{fcc}, \{112\}_\text{fcc} \) and \( \{001\}_\text{fcc} \) fiber texture. Metastable hexagonal close-packed (hcp)-Ni phase grains approximately 8.5 nm in size are also present, and there is compelling evidence that local texture of the predominant fcc-Ni phase facilitates the formation and resulting texture of the metastable counterpart.

Keywords: Precession electron microscopy; Nanostructured nickel; Texture; Metastable hcp phase

It is widely accepted that decreasing grain size into the nanoscale regime significantly influences the allotropic phase stability, melting temperature, as well as the mechanical, electrical and optical properties of metals and alloys [1,2]. In this regard, the concomitant instabilities in the microstructure of nanocrystalline metals contribute to abnormal [3–9] and mechanically induced grain growth [10–14], which further affect the aforementioned properties.

For the case of Ni, which typically exhibits a thermodynamically stable face-centered cubic (fcc) phase, in situ transmission electron microscopy (TEM) heating experiments on pulsed laser deposited (PLD) nanostructured Ni films have revealed unexpected phenomena during grain growth, such as the formation of stacking fault tetrahedra [15] and the presence of large metastable hexagonal close-packed (hcp)-Ni phase grains [16] that compete with and consume thermodynamically stable fcc-Ni phase. These in situ heating TEM studies raise fundamental questions related to the interplay between the microstructure and grain growth, namely: (i) are the metastable hcp-Ni phase grains present in as-deposited, unannealed PLD Ni films; (ii) how does the local texture influence the formation of hcp-Ni phase; and (iii) how do the metastable hcp phase grains compete with stable fcc phase grains?

Previous studies have reported metastable hcp-Ni phase [17–20] under various deposition and ion implantation [21] conditions, where oxygen contamination and athermal shear displacements were suggested to stabilize the metastable hcp phase. However, little is known about the hcp-Ni morphology, phase concentration or textural relationships with the stable fcc-Ni. Thus, the aforementioned questions have been difficult to address so far. In this work, we use precession electron microscopy to show that metastable nanoscale hcp-Ni phase grains are present in as-deposited, uncontaminated and unannealed nanostructured Ni films, and discuss their textural relationships with the stable fcc-Ni phase grains.

Ni films of nominal 50 nm thickness were deposited on NaCl crystals at room temperature by PLD, which is capable of producing dense, uncontaminated, nanostructured films [22]. A KrF laser (\( \lambda = 248 \) nm), with pulse width of 34 ns full-width half-maximum, a pulse rate of 35 Hz, and an energy density of 20 J cm\(^{-2}\) at the Ni target (99.997% Ni, Alfa Co., UK) was used to deposit Ni on the NaCl substrate at a rate of approximately 0.25 nm s\(^{-1}\). Subsequently, a few droplets of M-bond 610 (Vishay Precision Group, Rayleigh NC) epoxy were applied to the edges of thin bar 300 mesh TEM grids and placed on
the PLD-Ni films. To avoid sample heating, the epoxy was cured at room temperature for at least 1 day. The salt crystal below the film/grid assembly was then dissolved in a deionized water bath, and the remaining film/grid assembly was carefully lifted out of the deionized water and dried at room temperature.

These films were analyzed by performing precession electron diffraction with a near-parallel nanoscale probe (<5 nm in size), using a lens configuration similar to that in the diffraction–scanning transmission electron microscopy (D-STEM) technique [23]. The advantages of applying such a technique to nanostructured Ni films are several, namely: (i) a near-parallel nanoscale probe allows for a small interaction volume with the specimen resulting in high spatial resolution, (ii) a reduction in dynamic electron diffraction events due to decreased zone-axis channeling [24], and (iii) symmetry ambiguities are resolved due to the availability of a larger number of higher-order Laue zone reflections, all of which allow for accurate phase and texture characterization at the nanoscale [25]. The electron beam was precessed with an angle of φ = 0.40° and sequentially scanned, with a step size of approximately 1.8 nm, across the region of interest on the sample. These conditions result in a minimum resolvable grain ~4 nm in size.

Diffraction intensity data for the region of interest (~0.25 μm² per acquisition) was matched against kinematic diffraction intensity templates generated for fcc-Ni and hcp-Ni phases (a_{fcc-Ni} = 3.518 Å: JCPDS (Joint Committee on Powder Diffraction Standards) no. 458141, a_{hcp-Ni} = 2.651 Å, c_{hcp-Ni} = 4.343 Å: PDF (Powder Diffraction File) no. 00-045-1027) with angular resolution of 0.6° and 1.0°, respectively. On the basis of template matching and obtained correlation indices, the reliability of the identifiable phases was determined according to 1 – Q₂/Ｑ₁, where Q₁ and Q₂ are the highest and the second highest correlation indices, respectively [25]. Thus, for the condition of multiple grains present through the thickness of the film, the template matching algorithm recognizes the phase and orientation of the grain exhibiting the strongest diffraction signature and ignores the presence of the weaker grain.

For the present work, the generated phase and reliability maps were analyzed with image analysis software (Image J, National Institute of Health, Bethesda, MD) to determine the hcp and fcc phase contents, and corresponding grain sizes. Diffraction data from these films were also converted to orientation distribution functions from which color-coded inverse pole figure (IPF) maps and texture plots were obtained. A threshold misorientation angle of 5° was used to determine grain boundaries in the IPF maps. Furthermore, the obtained texture plots for these films were labeled in-plane (x- and y-axes) and out-of-plane (z-axis).

A bright-field TEM image of a representative region from the 50 nm Ni film is shown in Figure 1a. Although several nanoscale grains are visible in this image, dynamic electron scattering events, the presence of defects and off-zone axis grains severely limit the overall interpretation of the nanostructure. In contrast, the phase and reliability maps clearly show the morphology of the hcp-Ni and fcc-Ni phase grains in the film (Fig. 1b). Both hcp-Ni and fcc-Ni phase grains with distinct grain boundaries are visible. In this image, grains with maximum brightness are those whose diffraction intensities could be matched to the computer-generated diffraction templates for fcc or hcp phases with highest reliability. On the other hand, grain boundaries between two grains do not generate any interpretable diffraction intensity and therefore appear dark in the image. Diffraction data obtained during the precession acquisition from individual fcc-Ni and hcp-Ni grains were also independently indexed manually to confirm these results (Fig. 1c and d). The diffraction signatures appear to be strong and exhibit high reliability because these individual grains measure ~72 and ~53 nm in size (~4145 and ~2276 nm² projected area), respectively. Due to their relatively large sizes, it is assumed that these grains most likely traverse through the thickness of the 50 nm thick film.

Texture analysis indicates that the nanocrystalline Ni film is heterogeneous and comprised predominantly of (101)_{fcc} and (112)_{fcc} grains in the out-of-plane direction (Fig. 2a and b), with an in-plane (111)_{fcc} texture. The average fcc phase grain size is determined to be 22.0 ± 1.2 nm (95% confidence in the mean, assuming a normal distribution in 395 fcc grains). The black regions correspond to the metastable hcp phase grains that exhibit a (1010)_{hcp} out-of-plane texture (Fig. 2d) with a corresponding (0001)_{hcp} in-plane texture. 831 hcp-Ni phase grains were analyzed from an area of 0.75 μm² of the film, and these represent a phase fraction of 9% and an average grain size of 8.5 ± 0.3 nm (95%
Figure 2. (a) Inverse pole figure map from the 50 nm film, which exhibits a strong (101)$_{hcp}$/ND fiber texture. The black regions correspond to the hcp-Ni phase (inset shows the standard triangle for the fcc phase). (b) The corresponding texture plot for the fcc-Ni phase. (c) Inverse pole figure map for the hcp-Ni phase (inset shows the standard triangle for the hcp phase), which exhibits a strong (101)$_{hcp}$/ND. The black regions correspond to the fcc-Ni phase shown in (a). (d) Corresponding texture plots for the hcp-Ni phase (units for the texture scale are in multiples of random).

Figure 3. (a and b) Cropped and zoomed-in image obtained from Figure 2a and b, showing an hcp grain with a (101)$_{hcp}$ out-of-plane texture to be adjacent to fcc grains with (112)$_{fcc}$ and (101)$_{fcc}$ fiber texture.

A closer examination of Figure 2a and c, represented as zoomed-in and isometric images in Figure 3, show some edges of (101)$_{hcp}$ grains adjacent to fcc grains with (112)$_{fcc}$ (Fig. 3a), and (101)$_{fcc}$ out-of-plane texture (Fig. 3b), which hints at a possible textural relationship between hcp and fcc grains. Since the presence of certain out-of-plane textures results in the presence of specific in-plane textures, the observed (112)$_{fcc}$ and (101)$_{fcc}$ out-of-plane textures lead to a (111)$_{fcc}$ in-plane texture (Fig. 2a and b), as observed. With the available in-plane texture, the introduction of stacking faults on every other plane during PLD could lead to the formation of hcp-Ni phase grains with an in-plane (111)$_{fcc}$/〈0001〉$_{hcp}$ textural relationship. A hcp grain with an in-plane 〈0001〉$_{hcp}$ texture will have an out-plane 〈101〉$_{hcp}$ texture purely from crystallographic considerations, which is observed in this work (Figs. 2 and 3). Formation of stacking faults is expected to be relatively easy in these films despite the high stacking fault energy of Ni (∼125–300 mJ cm$^{-2}$) [26], since the PLD process imparts ∼20 J cm$^{-2}$ during deposition. These facts lead us to hypothesize that the hcp grains may be highly faulted fcc grains, as has been previously reported [15]. A simple calculation reveals that it requires ∼43 stacking faults on every other fcc plane to generate a 8.5 nm grain (previously determined hcp grain size in these films) that exhibits a hcp-type diffraction signature. Since this heavily faulted structure encounters other fcc grains of a different out-of-plane texture, it stops growing. This is a likely possibility because previously discussed grain size measurements indicate that stable phase fcc grains are approximately two and a half times (∼22 nm) larger than the metastable hcp phase grains. Finally, some hcp grains with a non (101)$_{hcp}$ out-of-plane texture adjacent to (112)$_{fcc}$ grains are also observed (Fig. 3). This is to be expected since, in cubic materials, only three (112)$_{fcc}$-type directions are orthogonal to (111)$_{fcc}$-type directions; not all (112)$_{fcc}$ directions lead to an in-plane (111)$_{fcc}$ texture, which we predict is conducive to the formation of texturally related fcc–hcp grains.

Indirect evidence for the aforementioned hypothesis is found by examination of other regions of the same film. Interestingly, these regions exhibit a strong 〈001〉$_{fcc}$ fiber texture with a significantly small fraction of grains with 〈101〉$_{fcc}$ and (112)$_{fcc}$ out-of-plane texture and no strong
grains are deficient in \{111\}_{\text{hfc}} texture and therefore exhibit approximately four times lower hcp-Ni concentration and hcp grains with relatively unstable fiber texture. These results lead us to believe that the local texture of the predominant fcc-Ni phase facilitates the formation and resulting texture of the metastable hcp-Ni phase during PLD of nanostructured Ni films.

We thank Mr. J. Kacher, Dr. B.G. Clark, Dr. B.L. Boyce and Prof. I.M. Robertson for valuable discussions and suggestions. This work was fully supported by the Division of Materials Science and Engineering, Office of Basic Energy Sciences, US Department of Energy, Sandia National Laboratories is a multi-program laboratory operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin company, for the US Department of Energy’s National Nuclear Security Administration under contract DE-AC04-94AL85000. We also acknowledge Nanomegas, Inc. for setting up the Precession Microscopy system at UT-Austin.

\[\text{(111)}_{\text{fcc}} \text{ in-plane texture (Fig. 4a and b). Although, the hcp-Ni grains in these regions exhibit } \{10\overline{1}\} \text{ fiber texture, and (b) the associated texture plot that shows negligible in-plane } \{111\}_{\text{fcc}} \text{ texture. (c) Inverse pole figure map of the corresponding hcp-Ni phase grains, and (d) its corresponding texture plot (units for the texture scale are in multiples of random).}\]

In conclusion, this work provides compelling evidence that hcp grains are present in pure as-deposited and unannealed nanostructured Ni films produced by PLD. Crystallographic observations suggest that grains with \{112\}_{\text{fcc}} \text{ and } \{101\}_{\text{fcc}} \text{ fiber texture result in an in-plane } \{111\}_{\text{fcc}} \text{ orientation, which is conducive to the formation of stacking faults during high-energy film deposition, leading to hcp grains with an in-plane } \{0001\}_{\text{hcp}} \text{ texture. However, regions with } \{001\}_{\text{fcc}} \text{ grains are deficient in } \{111\}_{\text{fcc}} \text{ texture and therefore exhibit approximately four times lower hcp-Ni concentration and hcp grains with relatively unstable fiber texture. These results lead us to believe that the local texture of the predominant fcc-Ni phase facilitates the formation and resulting texture of the metastable hcp-Ni phase during PLD of nanostructured Ni films.}\]