Synthesis, Thermal stability and Mechanical Behavior of Nano-Nickel

M.J.N.V. Prasad, P. Ghosh AND A.H. Chokshi

Abstract | Nanocrystalline materials exhibit very high strengths compared to conventional materials, but their thermal stability may be poor. Electrodeposition is one of the promising methods for obtaining dense nanomaterials. It is shown that use of two different baths and appropriate conditions enables the production of nano-Ni with properties similar to commercially available materials. Microindentation experiments revealed a four fold increase in hardness value for nano-Ni compared to conventional coarse grained Ni. An improved thermal stability of nano-Ni was observed on co-deposition of nano-Al_2O_3particles.

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1. Introduction

Conventionally, the plastic or permanent deformation of crystalline materials is related to the movement of line defects termed dislocations. The movement of dislocations is obstructed by grain boundaries in polycrystalline materials, across which there is a change in crystallographic orientation. Consequently, a decrease in grain size leads to an increase in strength, as given by the Hall-Petch equation [1]:

$$\sigma = \sigma_0 + K d^{-1/2} \tag{1}$$

where σ is the flow stress of a material with a grain size of d, σ_0 is the friction stress, and the constant K reflects the difficulty in slip transfer.

It follows from eqn. 1 that a reduction in grain size to the nanocrystalline regime offers a simple potential means for enhancing the strength of materials. Experiments indicate that nanometals with grain size of <100 nm exhibit substantially higher strengths compared to conventional materials with grain sizes of >10 μm. However, the synthesis of bulk dense nanocrystalline materials is challenging, and it is now recognized that the presence of pores and other defects can lead to variations in mechanical data. Several methods have been developed to obtain nanomaterials, including two step methods involving consolidation of nanoparticles synthesized by inert gas condensation or ball milling, or by one step methods such as severe plastic deformation (SPD) and electrodeposition[1,2]. However, the two step methods have been handicapped by residual porosity, impurities, and difficulty in processing of bulk samples whereas SPD methods produce quite inhomogeneous microstructure in terms of large number of subgrain boundaries and they also are unable to produce nanometals with grain sizes substantially <50 nm. Nanocrystalline metals and alloys with grain size down to 2 nm and even amorphous materials can be produced by electrodeposition with the use of pulse technique and/or addition of some organic compounds such as saccharin. By electrodeposition one can produce dense nanocrystalline materials with a narrow grain size distribution.

Synthesis of nano-materials by electrodeposition requires the formation of high nuclei density and the controlled growth of the deposited nuclei. The high nuclei density can be generated by supplying high d.c. current to the system; however, there is a possibility of depletion of metal ion source near substrate on continuous supply of high current. At the same time the continuous supply of d.c. current leads to columnar grain morphology in deposit. The

Table 1: Bath composition and deposition parameters

Watts bath	Sulfamate bath
$NiSO_46H_2O$ = 300 gpl	Ni $(SO_3NH_2)_2$= 400 gpl
$NiCl_2xH_2O$ = 45 gpl	$NiCl_2xH_2O$ = 45 gpl
H_3BO_3 = 45 gpl	H_3BO_3 = 45 gpl
Saccharin = 1–5 gpl	Saccharin = 1 gpl
Sodium lauryl sulfate = 0.1–0.4 gpl	Sodium lauryl sulfate = 1 gpl
Citirc acid = 0–5 gpl	pH = 4
Surfactant = 0–0.25 gpl	
Al_2O_3 nanoparticles ($\sim$ 40 nm) = 0–40 gpl	
pH = 3	

pulsed mode power supply facilitates use of high current during short on-time and the supply of fresh metal ions during off-time by stirring the solution. The intermittent power supply in pulsed mode also helps in preventing the formation of a columnar structure during deposition, leading to a more equiaxed three dimensional grain structure. Grain growth can be controlled using organic additives and/or adjusting suitable off-time. It has been observed that other deposition parameters such as temperature and pH also play a role in the formation of high nuclei density as well as in controlling growth of nuclei. During electrodeposition, grains tend to acquire a preferred orientation depending upon the processing variables (pH, current density, additives) used.

Grain boundaries, like surfaces, have higher energies than the bulk crystal. Therefore, a reduction in grain size to the nanocrystalline range provides a high driving force for grain growth. Consequently, the thermal stability of nanometals is an area of considerable concern for applications. It has been reported[3–5] that electrodeposited nano-nickel exhibits $<001>$ texture and also low thermal stability, with the development of abnormal coarse grains on annealing at $T > 473$ K. Several attempts have been made to improve thermal stability of nanometals by alloying or incorporating second phase particles. The incorporation of second phase particles during electrodeposition is also challenging.

The purpose of present investigation was to compare commercially available nano-Ni with materials synthesized in-house by pulsed electrodeposition using different electrolytes. The microstructure of all materials was characterized, and the thermal stability and mechanical properties were also examined. To evaluate the possibility of enhanced thermal stability in particle reinforced nanometals, a nano-Ni composite was also prepared by incorporating nano-Al_2O_3particles during electrodeposition.

2. Experimental Materials and Procedure

Commercial pulse electrodeposited nanocrystalline Ni (nano-Ni) foils with thickness about 150 μm were procured from Integran Technologies Inc. (Canada) with a reported grain size of 20 nm and purity of 99.8% of Ni with sulfur and carbon as major impurities. For comparison, a coarse-grained conventional nickel sheet with a thickness about 10 mm was obtained from Midhani (India) in the hot-rolled and annealed condition.

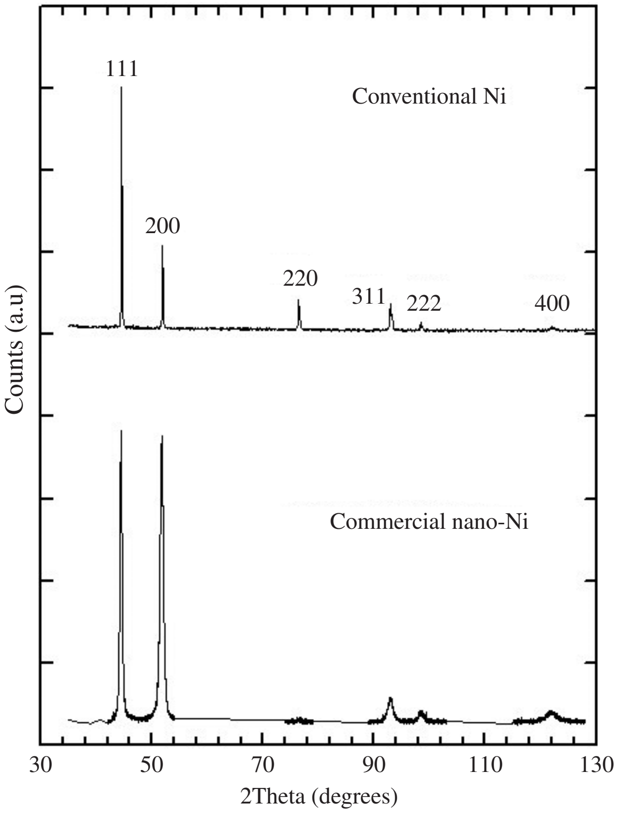
Nano-Ni foils of 25 × 25 mm with about 200 μm thickness were synthesized in-house by the pulsed electrodeposition method. The power supply for electrodeposition had a capacity of 10 V and 15 A, with variable on-time of 1 to 5 ms and off-time of 20 to 100 ms in five steps. Nickel sheets were used as anode and Titanium sheets were used as cathode (substrate). Two different types of electrolytes were used: Watts bath (sulfate) and sulfamate. Based on earlier reports and several initial experiments, the composition of electrolytes and deposition parameters used for producing nano-Ni are given in Table 1. Milli-Q-Pore water (ultra distilled water) was used for preparing electrolyte. Saccharin was added as a grain refiner and stress reliever, and sodium lauryl sulphate was added to minimize hydrogen evolution near substrate to limit porosity in the deposits. Co-deposition of nano-Al_2O_3 particles ($\sim$ 40 nm) along with Ni was carried out in the presence of a surfactant. Analytical grade chemicals obtained from Sigma-Aldrich were used. The pH of the solution was adjusted by ammonia hydroxide, nickel hydroxide and sulfuric acid solutions. Deposition was carried out under galvanostatic conditions with a constant current density of about 300 mA/cm^2. The temperature of bath was maintained at 323 K by circulating hot water through a specially designed double wall electrolytic cell.

The characterization of microstructure (grain size) was carried out using X-ray diffraction (XRD) peak broadening analysis (Warren-Averbach method), optical microscopy, transmission electron microscopy (TEM) and atomic force microscopy (AFM).

The variation of hardness in Ni as a function of grain size and the electrolytic bath was studied at room temperature by depth sensing microindentation. A Vickers diamond indenter was used with a maximum load of 1 N maintained for 15 s. The loading and unloading rates were 1 N/min. Typically, ten indentations were taken under each condition.

The as-received commercial nano-Ni and the as deposited (synthesized) nano-Ni were heated continuously at a heating rate of 10 K/min in differential scanning calorimetry (DSC). Commercial nano-Ni was annealed isothermally in an inert atmosphere at temperatures of 473 K and 573 K for 10 h.

Figure 1: XRD patterns of conventional coarse grained Ni and commercial nano-Ni.

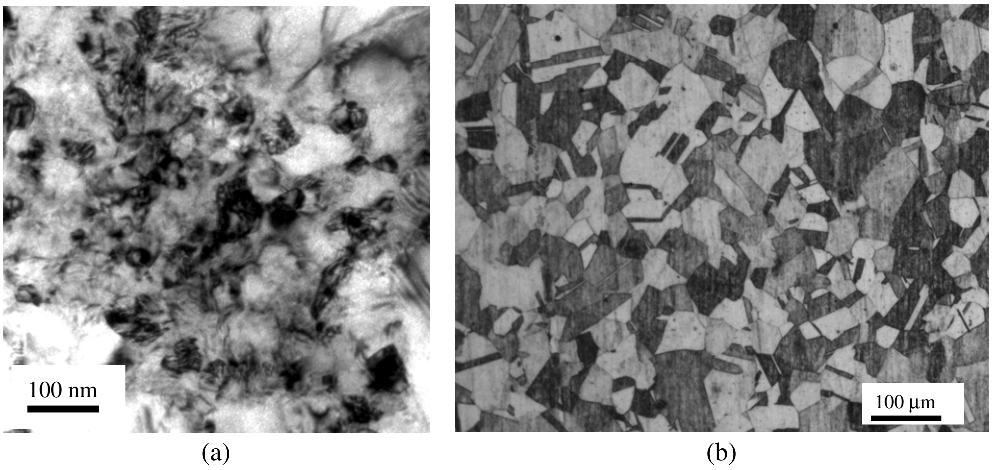


3. Results and Discussion

Figure 1 depicts the XRD pattern of the as received commercial nano-Ni, where peak broadening and peak intensities were compared with conventional coarse-grained Ni. It was observed that the ratio of integrated intensities of (111) and (200) peaks of commercial nano-Ni was about 0.8, compared with a value of 2.4 expected for a randomly oriented polycrystalline Ni. These results indicate that there is a strong <100> preferred orientation in electrodeposited Ni. In case of nano-Ni more peak broadening was observed. The (111)–(222) peak pair was used for Warren-Averbach (W-A) method to determine the grain size and microstrain of nano-Ni. Table 2 summarizes data for the commercial nano-Ni and synthesized nano-Ni in terms of the grain size, microstrain, hardness and elastic moduli. It is clear that the in-house synthesized material had a finer grain size than the commercial nano-Ni. Figure 2(a) shows a TEM micrograph of commercial nano-Ni whereas Fig. 2(b) is optical micrograph of conventional Ni. Grain sizes of commercial nano-Ni and conventional Ni were measured from micrographs by linear intercept method. Grain size of commercial nano-Ni determined from XRD by W-A (18 nm) was in good agreement with TEM measurements (∼19 nm).

Microindentation was carried out on selected samples. The hardness and elastic modulus were determined from load–displacement curves using the Oliver-Pharr method[6] are given in Table 2. Typical load–displacement curves for conventional Ni and nano-Ni are shown in Fig. 3. It was observed that elastic modulus of Ni obtained from different sources was essentially the same and close to the value of a randomly oriented polycrystalline Ni (205 GPa)[7]. The hardness of nano-Ni was almost four times that of conventional Ni. The plating bath

Figure 2: (a) Bright field TEM image of commercial nano-Ni and (b) optical micrograph of conventional Ni.



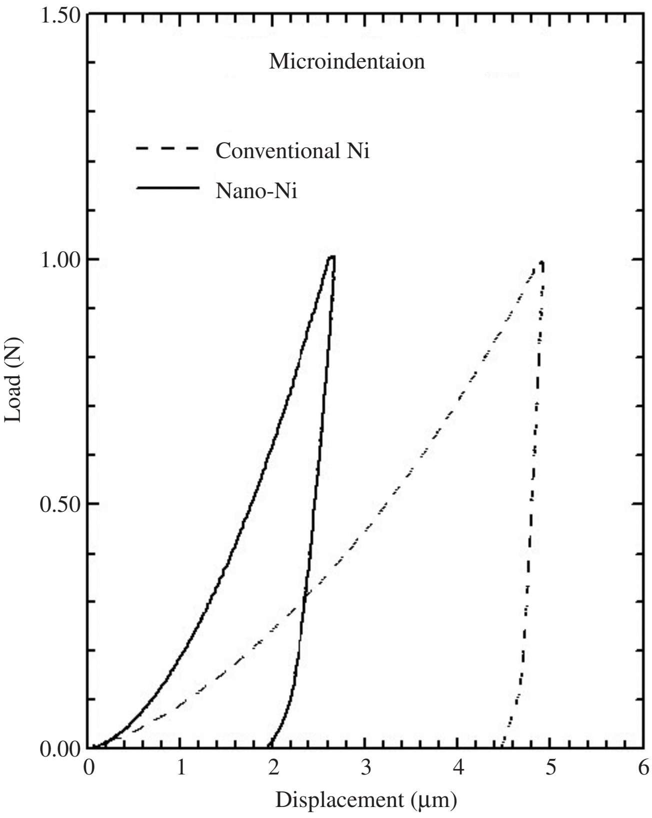
(a) (b)

Table 2: Grain size, microstrain, hardness and elastic modulus of Ni

Bath	Saccharin (gpl)	Grain size (nm) (XRD)	Microstrain ($\times 10^{-3}$)	Hardness (HV)	Elastic Modulus (GPa)
Conventional micro-Ni	–	50000#	–	162 ± 12	196 ± 15
Commercial nano-Ni	–	18	2.0	543 ± 8	187 ± 8
Watts	1	10	2.4	682 ± 10	191 ± 9
Sulfamate	1	10	2.6	697 ± 23	192 ± 5

#Optical microscope

Figure 3: Microindentation load–displacement curves for nano-Ni and conventional Ni.



did not appear to have any significant effect on strength or grain size. Furthermore, grain boundary strengthening was noted even in the nanocrystalline range, since the 10 nm material had a higher hardness than the 20 nm commercial nano-Ni.

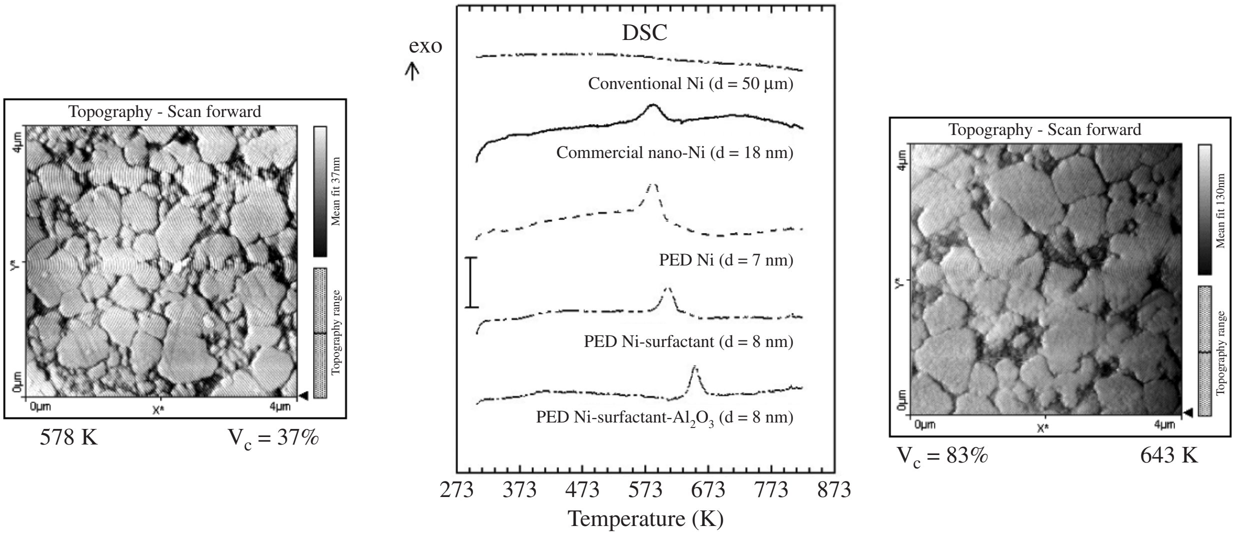
Figure 4 illustrates the thermal stability study of Ni from DSC experiments at a constant heating rate of 10 K/min. There are three observations from this study. First, an exothermic peak was observed for nano-Ni deposits obtained under different conditions which was absent for conventional coarse grained Ni, which indicates that the peak in nanometals is associated with grain growth. Second, an increased area under exothermic peak was observed for laboratory synthesized nano-Ni ($d = 10$ nm) compared to commercial nano-Ni ($d = 20$ nm), which is consistent with the respective grain sizes. Third, a shift in peak temperature towards higher side was observed in nano-Ni deposits obtained in the presence of surfactant (~ 20 K) as well as Al_2O_3 nano-particles (~ 50 K).

Microstructural examination of the commercial nano-Ni revealed abnormal grain growth with coarse grains (>200 nm) fraction (V_c) of about 37% in samples cooled rapidly from 578 K (near peak) and almost complete uniform coarse grains with about 83% coarse grains in samples cooled from 643 K (beyond peak). Thus, the observed exothermic peak can be attributed to abnormal grain growth. The area under peak is a measure of energy release during abnormal grain growth and it can be related to reduction in grain boundary energy on grain growth. Since the grain sizes of synthesized nano-Ni deposits were less than 10 nm, a higher energy release is anticipated compared to commercial nano-Ni whose grain size was about 20 nm. The shift in peak temperature with alumina particles suggests that the particles may be pinning grain boundaries and contributing to their additional stability. Isothermal annealing experiments on commercial nano-Ni also confirms abnormal grain growth process at 473 K (Fig. 5a) and the near-completion of grain growth leading to uniform coarse grains at 573 K (Fig. 5b).

4. Summary and conclusions

Nano-Ni foils with grain size of ~10 nm were synthesized by pulsed electrodeposition using Watts and sulfamate electrolytic baths. There was no effect of electrolytic bath on grain size. The in-house fabricated samples had a finer grain size than the commercial nano-Ni foils. The hardness of the nanometals were substantially higher than the conventional coarse grained samples. An improved thermal stability was observed in nano-Ni composites containing Al_2O_3 particles.

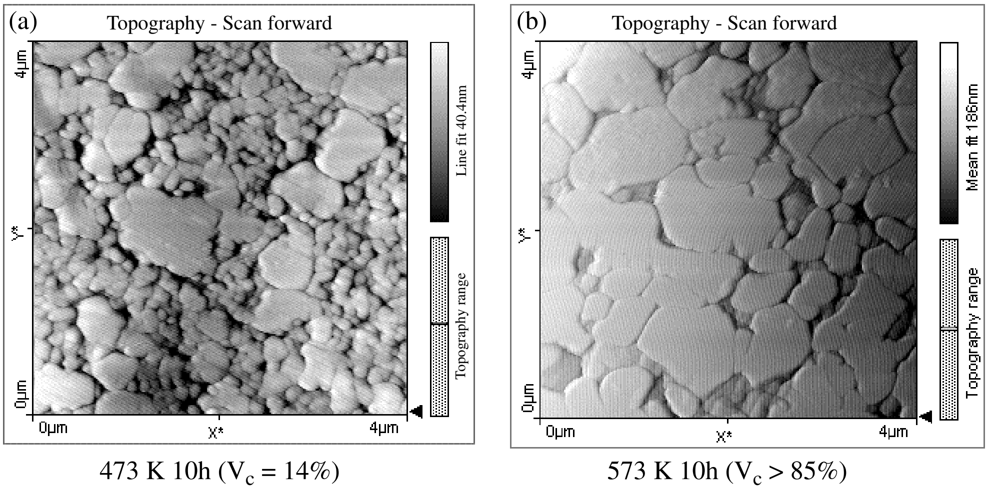
Figure 4: A DSC plot for Ni under different conditions together with AFM images of commercial nano-Ni heated to 578 K (left) and 643 K (right) at 10 K/min. *V* is the volume fraction of coarse grains.



578 K $V_c = 37\%$

$V_c = 83\%$ 643 K

Figure 5: AFM images of commercial nano-Ni isothermally annealed at (a) 473 K and (b) 573 Kfor 10 h.



473 K 10h ($V_c = 14\%$)

573 K 10h ($V_c > 85\%$)

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