High strength and high ductility in as-deposited nanocrystalline Ni

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Abstract. In the present study, an electrodeposited nanocrystalline (nc) Ni sample with high strength and superior ductility relative to many other electrodeposited nc-Ni was prepared. The superior ductility in the present nc-Ni sample free of defects was ascribed to mixed grains, the size of which spanned nano- and sub-micro scales at its as-deposited state with a grain size distribution ranged from 5 to 120nm. Obvious dislocation motion happening in coarse-grained polycrystalline was observed in large grains of nc-Ni matrix resulting in a remarkable enhanced ductility without a decrease in the strength. The present nc-Ni with an average grain size of 27.2nm prepared by direct current electrodeposition shows the average ultimate tensile strength of 1200MPa and the average elongation to failure of 10.4%.

1. Introduction
Nanocrystalline (nc) materials with high strength and high hardness, are expected to be new generation engineering structural materials, but to obtain the higher ductility must be the premise of practice applications. In the past decade, deformation mechanisms in nc materials were extensively investigated through experimental studies and molecular dynamics (MD) simulations. Some new deformation mechanisms including partial dislocations emission from grain boundaries (GB) [1], deformation twin [1-2], grain rotation [3], GB migration [4] have been well-proposed. However, the direct relationship between deformation mechanisms and associated mechanical properties, especially for the ductility, is not fully understood yet. Nonetheless, some effective routes have been suggested to improve the ductility of nc materials [5-8]. One of these routes was focused on the microstructure design, e.g. a composition of nanoscale grains and ultrafine grains (UFGs) (100-500nm) [5,7]. This method relies on the nc matrix to hold the high strength but increases the ductility by introduction of the conventional dislocation sliding to large grains. According to the characteristic of nc materials having abnormal grain growth, the bimodal microstructure can be obtained by thermal annealing. For electrodeposited nc metals, however, low temperature annealing always causes embrittlement [9]. In the present study, a nc-Ni sample prepared by electrodeposition with a broad grain size distribution (BGSD nc-Ni) was reported. The nc-Ni sample has the upper limit of grain size over 120nm but with an average grain size of 27.2nm in the as-deposited statement. The combination of high strength and good ductility was obtained for the BGSD nc-Ni sample. The intracrystalline dislocation network
was observed in the post-deformed microstructures confirming the conventional intracry stalline dislocation sliding mechanism.

2. Experimental procedure
In the present study, an aqueous sulfamate-based electrolyte was used to produce BGSD nc-Ni by direct current electrodeposition. The electrolyte was made of 500g L⁻¹ Ni(NH₂SO₃)₂·4H₂O, 20g L⁻¹ NiCl₂·6H₂O, 30g L⁻¹ boric acid, 15g L⁻¹ MnCl₂·6H₂O, 2.5g L⁻¹ soluble saccharin and 0.1g L⁻¹ lauryl sodium sulfate. The main electrodeposition conditions are listed in Table 1. Under these conditions, BGSD nc-Ni, the thickness of which was 180-200 μm, was deposited on the stainless steel substrate, which had been polished to a mirror-like finish surface prior to electrodeposition. After electrodeposition, the deposits can be mechanically stripped from the stainless steel.

The composition of the BGSD nc-Ni was detected by X-ray Fluorescence (XRF). The microstructures of BGSD nc-Ni were observed by transmission electronic microscope (TEM). TEM observations were performed using a Tecnai G2 F20 S-TWIN operated at 200KV. TEM samples were prepared by double-jet electropolishing using an electrolyte consisting of 5 vol.% perchloric acid and 95 vol.% ethanol at a temperature below -20°C. The average grain size was determined from dark field TEM images using the image analysis software (Photoshop 7.0) to count at least 500 grains for each sample.

The dog bone shaped tensile specimens of BGSD nc-Ni with a gauge length of 10mm and gauge width of 6mm were cut using the electro-discharging machine. Room temperature (RT) tensile tests were carried out with the strain rate varying from 5×10⁻⁵ s⁻¹ to 10⁻² s⁻¹.

| Table 1. The main condition for preparing BGSD nc-Ni |
|------------------------------------------------------|
| Electrolyte volume (L) | 1 |
| Electrolyte temperature (℃) | 60 |
| pH | 3.5 |
| Current density (A/dm²) | 8 |
| Anode material | Electrolytic Ni (purity > 99.9 mass.%) |
| Ratio of cathode area to anode area in the plating bath | 1:4 |
| Cathode substrate | Stainless steel sheet (1Cr15Mo8Ni5Cu2) |

3. Results and discussion.
The TEM bright field image of as-deposited nc-Ni sample is shown in figure 1(a). It is observed that isolated large grains with the size of 120nm are surrounded by small grains with the size below 30nm forming an inhomogeneous microstructure, which is similar to grains undergone abnormal growth in the low temperature annealing. Some defects e.g. dislocation, twin or sub-grain boundary, marked by black arrows, are clearly seen within large grains. The inset is a typical ring pattern further confirming that the global grain size is in the nanoscale. The statistical diagram (figure 1(b)) shows that the BGSD nc-Ni sample has an average grain size of 27.2nm with a grain size distribution ranging from 5 to 120nm. No Mn was detected in the nc-Ni though there was MnCl₂ in the electrolyte. The MnCl₂ affects the deposition process and results in a broad grain size distribution in the deposits.

The engineering stress-strain curves for BGSD nc-Ni are shown in figure 2(a). The average 0.2% offset yield strength, σ₀.₂, is 638MPa and the average ultimate tensile strength, σₜₚₚₚ, is 1176MPa. The average elongation to fracture, δₑₚₑₑ, is 10.6%. In comparison with nc-Ni with a relatively narrow grain size distribution (NGSD) of 10-50nm and an average grain size of 15-25nm, which has a σₜₚₚₚ of 1200-1300MPa and a common ductility with δₑₚₑₑ of 4-5% [9-10], apparently, the present BGSD nc-Ni samples possess the markedly enhanced ductility and the similar strength.
Figure 1. TEM bright field image (a) and grain size statistical distribution (b) for electrodeposited nc Ni with a broad grain size distribution.

Figure 2. Engineering stress-strain curves

Figure 3(a) shows a TEM bright field image from the tensile fracture of BGSD nc-Ni. Apparent grain growth is observed in contrary to the as-deposited grain size in figure 1(a). In comparison with figure 1(a), the statistical analysis in figure 3(b) displays that the average grain size after deformation is increased by 19.3nm and that there is a sharp decrease in the number fraction of sizes below 30nm. In addition, few large grain coalescences with sizes over 200nm are also observed in the post-deformed microstructures, as shown in figure 3(c). These observations indicate the propensity of grain growth driven by applied stresses in BGSD nc-Ni is stronger than that of NGBD nc-Ni [3,4,11]. It seems that the large grains can act as cores to merge neighboring small grains by grain rotation [3,11] forming the grain coalescence during plastic deformation. In addition, dislocations trapped in the grain coalescence and dislocation pile-ups at GBs are observed. One of these phenomena was captured in figure 3(c). These findings offer compelling evidence to support the conventional intracrystalline dislocation-sliding mechanism dominated in BGSD nc-Ni.

It was pointed that dislocations are hardly to move in small nanograins due to the need of very high stress to activate dislocation sources, e.g. the Frank-Read source [12]. The critical stress, \( \tau \), to activate the Frank-Read source can be expressed as \( \tau = \frac{G b}{L} \), where G is shear module (80GPa for Ni), b the smallest Burgers vector in face-centered cubic metals (0.249nm for Ni) and L the distance between two pinning points (typical L=d/3 or d/4 and d is the grain diameter). According to the equation, for grains of sizes of 80-120nm, \( \tau \) is estimated about 498-746MPa, which is close to the present experimental yield stress. Accordingly, the Frank-Read source can be activated in the large grains of sizes over 80nm in the practical tensile deformation. Moreover, grain growth in the plastic...
deformation process may further favour the activation of the Frank-Read source with increasing deformation strains.

Figure 3. TEM images of deformed BGSD nc-Ni and the statistical analysis of grain size. (a) typical image showing pronounced global grain growth, (b) statistical grain size distribution after deformation, (c) image showing significant grain growth and pile-ups of dislocation ahead of grain boundaries after deformation.

Conclusion
(1) In comparison with typical NGSD (10-50nm) nc-Ni, with an average grain size of 15-25nm, has a common ductility with $\delta_{ETF}$ of ~4% and a high strength with $\sigma_{UTS}$ of 1200-1300MPa at room temperature and strain rates of $3\times10^{-3}$ or $10^{-4}s^{-1}$. However, the present BGSD (10-120nm) nc-Ni sample prepared by direct current electrodeposition with an average grain size of 27.2nm exhibits a considerable ductility (over 10% of $\delta_{ETF}$) along with the similar strength.
(2) The intracrystalline dislocation network was observed in the post-deformed microstructure confirming the conventional intracrystalline dislocation sliding mechanism in BGSD nc-Ni.

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