Electrodeposited Nanocrystalline Nickel Dispersed with Nano-Size WO₃ Particles

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A new class of bulk nanocrystalline nickel dispersed with nano-scale WO₃ particles has been synthesized by conventional electrodeposition. It was found that WO₃ particles of an initial size of 0.1 μm, when suspended in an electrolyte, fragmented into smaller nano-scale particles during deposition accompanied by phase transition from an initial monoclinic to tetragonal structure. The cause and effect relation between the fragmentation and the phase transition of WO₃ particles was discussed. Hopefully, the phenomenon can be applied to establish a novel synthesis for a new class of bulk nanocrystalline metals with dispersed nano-scale particles endowed with higher strength and thermal stability than conventional mono-phase nanocrystalline materials. [doi:10.2320/matertrans.M2012013]

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1. Introduction

Bulk nanocrystalline metallic materials have very high strength and are promising materials for future structural applications. With regard to the deformation mechanism of bulk nanocrystalline metals which have been discussed extensively, additional strengthening by fine dispersions in nanocrystalline metals are of increasing interest.^{1–3)} For example, additive strengthening by Orowan-type dislocation-particle interaction and the Hall–Petch effect in nanocrystalline materials has been discussed.¹⁾ In addition to their strengthening, such very fine particles can stabilize the nanocrystalline structure whose low thermal stability is a drawback of nanocrystalline materials and has limited their industrial application in spite of very high interest in the scientific community.⁴⁾ Particle dispersions or precipitates to pin grain boundaries are common kinetic approaches to stabilize the structures. According to classical Zener drag theory, the stabilized grain size d , is given by $d = 0.66\phi/f$ where ϕ is particle size, and f is volume fraction,⁵⁾ which suggests that very fine particles of about 4 nanometers are required to disperse homogeneously in order to stabilize nanocrystalline structures with a grain size of 50 nm (if the volume fraction f is 0.05). Such finely dispersed nanocrystalline metals have been very difficult to synthesize or fabricate by conventional methods. Ultrafine-grained aluminum alloys fabricated by severe plastic deformation, such as ECAP, have been stabilized by subsequent aging treatment.^{6,7)} However, in this processing, one cannot avoid a certain amount of grain growth and Ostwald ripening of the precipitate during the ageing treatment. In the consolidation of mixed powders by mechanical alloying or ball-milling, fine particles tend to aggregate during the mixing the process.⁸⁾ This trend becomes stronger with decreasing powder size due to the greater surface energy. Another method of synthesizing bulk nanocrystalline metals is electrodeposition, which is, from a synthesis point of view, one of the oldest methods used to produce nanostructured materials.⁹⁾ Nanocrystalline metals dispersed with hard particles have generally been plated using an electrolyte with suspended hard particles such as

SiC,¹⁰⁾ Al₂O₃,¹¹⁾ TiO₂,¹²⁾ SiO₂.¹³⁾ Similarly, particle size has been limited to larger than several microns in order to avoid agglomeration of particles during the synthesizing.

In an effort to synthesize nanocrystalline nickel with dispersed very fine particles, the authors discovered that WO₃ particles suspended in an electrolyte were fragmented into finer particles accompanying phase transition from a monoclinic to a tetragonal structure during electrodeposition. Hopefully, the phenomenon can be applied to establish a novel synthesis for a new class of bulk nanocrystalline metals with dispersed nano-scale particles having higher strength and thermal stability than conventional nanocrystalline materials.

2. Experimental Procedures

Dispersed nanocrystalline nickel was plated by electrodeposition in a sulfamate bath (nickel sulfamate 50 g/L, nickel chloride 10 g/L, boric acid 30 g/L, saccharin, 2 g/L, sodium dodecyl sulphate 0.5 g/L, pH = 4). Commercially available WO₃ particles with an average diameter of about 0.1 μm were suspended at a rate of 1.9 g/L in the electrolyte.

Deposition was carried out using a pulse plating power supply (Hokuto Denko Co., HCP-301H) at a bath temperature of 50°C. In order to avoid agglomeration of WO₃ particles, dispersion in the bath was assisted by an ultrasonic disperser for 30 min before and during plating. During deposition, the plating bath was stirred by a magnetic stirrer with a rotation speed of 360 rpm. A rectangular AISI304 and nickel plates with an area of 30 cm² were used as the cathode and anode electrodes, respectively. The depositions were carried out with a current density of 150 mA/cm².

Microstructures of the deposits were examined by transmission electron microscopy with energy dispersion spectroscopy (FE-TEM with EDS, JEOL JSM 2100F). X-ray diffraction (XRD) analysis was performed on a Rigaku RINT2500 X-ray diffractometer using Co-K α radiation.

3. Results and Discussion

XRD spectra of as-electrodeposited and original WO₃ powders are compared in Fig. 1. In the former spectrum, the diffraction peaks of the second phase in addition to Ni can

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Fig. 1 XRD patterns of the (a) nanocrystalline Ni with WO₃ dispersions and (b) original WO₃ particles.

be recognized, and they seem to correspond with those of the tetragonal structure of WO₃. On the other hand, diffraction peaks of the original WO₃ particles indicate that they are mainly monoclinic structures partially coexisting with the tetragonal structures. These two XRD spectra indicate that WO₃ particles transformed from a monoclinic to a tetragonal structure during precipitation in the plating process. It is known that WO₃ has many (at least seven) polymorphs, and numerous complex stoichiometric and nonstoichiometric compositions such as WO_{3-x}, W₁₈O₄₉, W₂₀O₅₈, WO₂, and W₂O₅. The crystallographic structure of WO₃ is reported in the literature to progress through the following series of phase transitions upon heating: monoclinic (ϵ -WO₃) $\rightarrow$ triclinic (δ -WO₃) $\rightarrow$ monoclinic (γ -WO₃) $\rightarrow$ orthorhombic (β -WO₃) $\rightarrow$ tetragonal (α -WO₃).¹⁴ Therefore, the tetragonal structure observed in as-deposited plate is in a state of disequilibrium at room temperature. The mechanism of phase transition from monoclinic to tetragonal is not clear yet, but instantaneous temperature rise by deposition current cannot be ruled out. Second possibility is partial reduction by rapid potential drop. According to the *E*-pH diagram of W-H₂O system, WO₃ is supposed to be deoxidized to W below the equilibrium potential of Ni $\rightarrow$ Ni²⁺ + 2e⁻ (-0.257 V_{SHE}). However, there are several different compositions, such as W₂O₅ and WO₂, between WO₃ and W regions. During the carbon-reduction process, the WO₃ structure reportedly transforms into nonstoichiometric Magneli phases W₄₀O₁₁₈, WO_{2.9}, and finally to WO₂ and W.¹⁵ Therefore, it may be possible that, during rapid potential drops, particles are deoxidized to more complex stoichiometric or nonstoichiometric compounds near WO₃, which induces disequilibrium

Fig. 2 Original WO₃ particles observed by (a) SEM, and (b) bright-field TEM.

phase transition. The rigorous composition of the supposed WO₃ is not confirmed yet. Further study is required to clarify the mechanism in detail.

Figure 2 shows SEM and bright-field TEM images of original WO₃ particles. As shown in Fig. 2(a), particles with an average size of 10 μ m consist of smaller agglomerated particles with an average size of 0.1 μ m. Most of these particles were single crystals, or consisted of, at most, a few grains since grain boundaries were rarely observed inside particles as shown in Fig. 2(b). Figure 3(a) shows the bright-field image of nanocrystalline structure of as-electrodeposited nickel with an average grain size of 45 nm. Most importantly, very fine particles, smaller than 10 nm were observed to be embedded inside the grains as shown in Fig. 3(b). EDS spot analysis of precipitates shows the peaks of W and O elements, thus, they are again confirmed as tungsten oxide [Fig. 3(c)]. If one compares the original particles with embedded particles in electrodeposited plate, it is apparent that the particles became smaller during plating process. Figure 4 shows the diffraction pattern and corresponding dark-field image. Most of the diffraction spots inside the Ni (110) ring were identified as those of tetragonal WO₃ as indicated by the arrows. By activating several diffraction spots, very fine particles smaller than 10 nm are recognized in the dark-field image. However, several spots do not correspond with tetragonal WO₃, suggesting that a certain fraction of particles was transformed into different unidentified structures such as triclinic (δ -WO₃) and orthorhombic (β -WO₃), etc. They may transform to amorphous WO₃ by rapid heating over 250°C as reported by Habazaki *et al.*¹⁶ Since ICP analysis of W in the plate is 0.87 mass%, the volume fraction of WO₃, *f* is about 0.81%. Mean inter-particle spacing λ is given by $\lambda = (4\pi/3f)^{1/3} \phi/2$. Substituting $\phi = 10$ nm as the mean particle diameter in the equation, then $\lambda = 40$ nm, which seems smaller than that by the TEM observation. The discrepancy may arise from inhomogeneous distributions of the WO₃ particles and 2-dimensional observation by TEM.

The mechanism of fragmentation of WO₃ particles is not clear, but it may be associated with the phase transition from monoclinic to tetragonal structures during electrochemical reaction at the electrode. Phase transition of metal oxides generally induces internal strain and stress, and vice versa. Constrained phase transition produces very high strain and stress, which may cause crack initiation and fracture.¹⁷ A well-known example is ZrO₂, which cracks during phase transition from a monoclinic to isomeric structure at 1100°C.

Fig. 3 Observation of as-electrodeposited nanocrystalline nickel by (a) TEM bright-field image, (b) TEM bright-field image showing WO_3 particles inside grains smaller than 10 nm, and (c) EDS spectrum by spot analysis of the nano-scale particle indicated by the arrow 002 in (b).

Fig. 4 TEM observation by (a) a diffraction pattern of both Ni and WO_3 . Arrows indicate diffraction spots identified as tetragonal WO_3 . (b) dark-field image showing WO_3 particles dispersed in nanocrystalline Ni.

The volume expansion of unit cells from monoclinic to tetragonal structures in WO_3 is about 5%,¹⁴⁾ which should cause internal strain and stress during partial transformation. Rapid temperature rise and thermal strain during deposition is another possible cause of fragmentation of WO_3 particles. Once the particles are fragmented by thermal strain into those smaller than 10 nm, tetragonal structures can be stable at room temperature by size effect as reported by Boulova and

Lucazeau.¹⁸⁾ In this case, the cause and effect relation between the fragmentation and phase transition is opposite.

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REFERENCES

- 1) D. G. Morris and M. A. Morris: *Acta Mater.* **39** (1991) 1763–1770.
- 2) R. O. Scattergood, C. C. Koch, K. L. Murty and D. Brenner: *Mater. Sci. Eng. A* **493** (2008) 3–11.
- 3) K. V. Rajulapati, R. O. Scattergood, K. L. Murty, Z. Horita, T. G. Langdon and C. C. Koch: *Metall. Mater. Trans. A* **39** (2008) 2528–2534.
- 4) U. Klement, U. Erb, A. M. El-Sherik and K. T. Aust: *Mater. Sci. Eng.* **203** (1995) 177–186.
- 5) C. Zener: *Trans. AIME* **15** (1948) 175.
- 6) Z. Horita, K. Ohashi, T. Fujita, Y. Kaneko and T. G. Langdon: *Adv. Mater.* **17** (2005) 1599–1602.
- 7) J. K. Kim, H. G. Jeong, S. I. Hong, Y. S. Kim and W. J. Kim: *Scr. Mater.* **45** (2001) 901–907.
- 8) Y. Li, Y. H. Zhao, V. Ortolan, W. Liu, Z. H. Zhang, R. G. Vogt, N. D. Browning, E. J. Lavernia and J. M. Schoenung: *Mater. Sci. Eng. A* **527** (2009) 305–316.
- 9) U. Erb: *Can. Metall. Q.* **34** (1995) 275–280.
- 10) F. Hu, K. C. Chan and N. S. Qu: *J. Solid State Electrochem.* **11** (2007) 262–272.
- 11) A. Jung, H. Natter, R. Hempelmann and E. Lach: *J. Mater. Sci.* **44** (2009) 2725–2735.
- 12) J. Li, Y. Sun, X. Sun and J. Qiao: *Surf. Coat. Tech.* **192** (2005) 331–335.
- 13) H. Miyamoto, K. Ueda and T. Uenoya: *Mater. Sci. Forum* **654–656** (2010) 1162–1165.
- 14) T. Vogt, P. M. Woodward and B. A. Hunter: *J. Solid State Chem.* **144** (1999) 209–215.
- 15) A. A. Mohammad: *Acta Phys. Polonica A* **116** (2009) 240–244.
- 16) H. Habazaki, Y. Hayashi and H. Konno: *Electrochim. Acta* **47** (2002) 4181–4188.
- 17) D. R. Clarke, V. Sergo and M.-Y. He: *Elev. Temp. Coat. Sci. Tech.* **3** (1999) 67.
- 18) M. Boulova and G. Lucazeau: *J. Solid State Chem.* **167** (2002) 425–434.