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Full Length Article

Electrodeposition of nanocrystalline nickel embedded with inert nanoparticles formed via inverse hydrolysis

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ABSTRACT

Nanocrystalline electrodeposits embedded with inert hard nanoparticles are applied to coating on engineering materials for high hardness and thermal stability. They have mainly been synthesized from a solution containing a suspension of particles in electrodeposition. In this conventional synthesis, finer particles tend to agglomerate in the electrolyte and are embedded inhomogeneously in the electrodeposits. This work provides a different approach to synthesizing nanocrystalline metal electrodeposits embedded with inert metal oxide particles that are formed through inverse hydrolysis in an electrolyte before embedding in the electrodeposits. In principle, this approach would allow the embedding of particles ranging, in size, from the molecular to the micron scale through control of the pH and the duration of stand-by reaction prior to electrodeposition. Effect of this approach on the hardness and thermal stability of Ni electrodeposits was validated, and agree semi-quantitatively with theoretical values predicted by Orowan strengthening and Zener pinning, both of which assume that dispersed particles are smaller than the matrix grain size.

1. Introduction

Electrodeposition is a low-cost, effective method for synthesizing hard metallic materials that can be applied to free-standing structural materials or coating on engineering materials. Composites incorporating hard inert particles in nanocrystalline structure are the most common form of hard materials obtained by electrodeposition [1]. In particular, nanocomposites with nanoparticles embedded in nanocrystalline matrices exhibit not only extra hardening but also high corrosion [2–4] and wear resistance [2–8]. The term *nanocomposite* is often misleading in light of the strengthening mechanism, because nanosize particles with low volume fraction can serve as obstacles to dislocations, making the matrices harder, rather than share the stress with the matrices by the rule-of-mixture [9–12]. Such nanosize particles have an another benefit: they can stabilize kinetically nanocrystalline structures by pinning grain boundaries [13–15]. According to classical Zener pinning theory [16], the stabilized grain size, d, is given by $d = 4r/f$, where r is the particle radius, and f is the volume fraction of the particles. This well-known formula predicts that very fine particles of about 4 nm are required to disperse uniformly in order to stabilize nanocrystalline structures with a grain size of 50 nm ($f = 0.05$).

In electrodeposition, the synthesis of nanocomposite materials with embedded particles small enough for Zener pinning effect is typically conducted by one of two general approaches. One is the electrodeposition of supersaturated materials such as Ni-P [14,15,17–19], Ni-W [20], and Co-P [21,22] alloys, and subsequent aging treatment upon which Ni_3P, Ni_3W or Co_2P form fine, uniformly distributed precipitates, causing precipitation hardening. The effect of the precipitates on thermal stability is evident [14], but may be limited because the particles are reactive with the matrices, and tend to coarsen by Ostwald ripening at moderate or high temperatures [18].

The second approach involves the codeposition of inert nanoparticles using an electrolyte containing a suspension of nanoparticles. Electrodeposition of a variety of nanocomposites with inert nanoparticles has been reported, such as Ni-SiC [2,8–12,23,24], SiO_2 [25], Al_2O_3 [4,6,26–29], ZrO_2 [30], WO_3 [31], TiO_2 [3,7,32], diamond [33]. Inert particles are not reactive with the matrices, and would thus be expected to have a higher effect on the thermal stability. While the effect of the second approach on the hardness and wear resistance is evident and established, the effect on the thermal stability or resistance to grain growth has been little reported to date [34]. The reason for this may lie in the low uniformity or dispersibility of the embedded particles caused by agglomeration of the particles in the electrolyte [7].

The present work overcomes the above problem in the

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Table 1
Chemical composition of the electrolyte (g/L).

$Ni(SO_3NH_2)_2{\cdot}4H_2O$	500
$NiCl_2{\cdot}6H_2O$	10
H_3BO_3	30
$C_7H_5NO_3S$	2
$Na_2WO_4{\cdot}2H_2O$	20–200

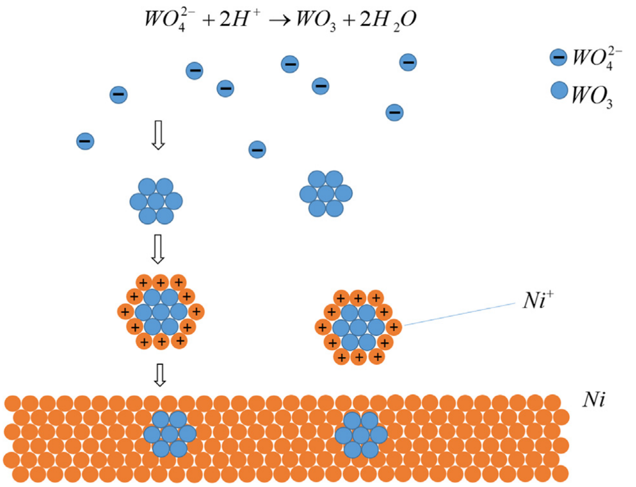

Fig. 1. Codeposition mechanism of WO_3 nanoparticles and Ni electrodeposit at the cathode plate.

electrodeposition by an approach that enables the synthesis of nanocrystalline Ni embedded uniformly with inert nanoparticles. In this approach, WO_3 particles that form from $WO_4{}^{2-}$ ions in the electrolyte by inverse hydrolysis are embedded in the nanocrystalline Ni electrodeposits. The WO_3 particles size can potentially be varied from the molecular scale to the conventional microscale by controlling the amount of $WO_4{}^{2-}$, the pH and the duration of stand-by reaction. The effect of the presence of nanoparticles (smaller than the grains) on both strength and thermal stability are demonstrated. This approach can potentially be applied to other oxide of metals such as Mn, V, Cr, Mo, etc.

2. Materials and methods

2.1. Electrodeposition

Nickel sulfamate bath solutions (Table 1) were prepared with different amounts of sodium tungsten (Na_2WO_4-$2H_2O$) ranging from 20 to 200 g/L. Na_2WO_4-$2H_2O$ was electrolyzed into Na^+ and $WO_4{}^{2-}$. According to the equilibrium diagram of the W–H_2O system, the inverse hydrolysis reaction occurred in the acidic electrolyte as follows,

$$WO_4{}^{2-} + 2H^+ \rightarrow WO_3 + H_2O \tag{1}$$

The $WO_4{}^{2-}$ ion formed WO_3 molecules, coalesced into particles, and became embedded in the Ni electrode during electrodeposition (Fig. 1). The above reaction was set to proceed for varying stand-by time prior to the onset of electrodeposition. The size of the embedded particles was controlled by varying Na_2WO_4-$2H_2O$ content, pH and stand-by time prior to electrodeposition. In order to confirm the formation of WO_3 particles in the electrolyte, the particles were collected from the solution by evaporating the electrolyte, and observed by transmission electron microscopy (TEM). The preliminary test revealed that the WO_3 particles formed and grew exponentially in the electrolyte after a certain incubation time as mentioned in the subsequent section.

In electrodeposition, pure nickel and copper were used as the anode and cathode, respectively. The current density was set at 30 mA/cm^2 and electrodeposition was conducted for 24 h at a pH of 0.5 and a temperature of 50 °C to obtain Ni-WO_3 electrodeposits with a final thickness of about 0.6 mm.

2.2. Material characterization

The microstructure of the electrodeposited Ni–WO_3 was observed by a field-emission transmission electron microscope (FE-TEM, JEOL JEM-2100F) equipped with an energy dispersive spectroscopy (EDS) system. A micro Vickers hardness tester (Shimadzu Co., HMV-2) was used to measure the hardness of the Ni-WO_3 electrodeposits. To identify the structure of the WO_3 particles formed during the stand-by time, X-ray diffraction (XRD) was performed on the collected WO_3 particles with a Rigaku RINT 2500 X-Ray diffractometer using Co Kα radiation.

3. Results

3.1. Characterization of WO_3 particle derived by the stand-by reaction

Fig. 2a shows TEM micrographs of collected WO_3 particles formed via an inverse hydrolysis reaction during the stand-by period prior to electrodeposition. They were collected from the evaporated electrolyte. The elements in the particle were identified as W, O, Ni and S (see Fig. 2b-c). Ni and S may have originated from the electrolyte. EDS spectra of the O and W in a particle showed atomic percentages of 78.0% and 22.0%, respectively, indicating that the particle was WO_3.

XRD analysis of the collected WO_3 particles after different stand-by inverse hydrolysis times is shown in Fig. 3. XRD spectra of commercial WO_3 powders of the monoclinic (γ) structure with a nominal diameter of 0.1 μm are also shown for comparison. For stand-by periods of 1–24 h, the crystal structures were mostly monoclinic (γ-phase), but small peaks of other unidentified phases were observed as well. After 336 h, the particles were almost exclusively monoclinic, with very small peaks of other structures. WO_3 has numerous polymorphs with its structure changing with temperature and particle size [35,36]. Monoclinic (γ) is the most stable phase at room temperature for particles larger than 500 nm, but orthorhombic (β) and tetragonal (α) phases appear at higher temperatures and for smaller particles [35,36]. Fig. 4 shows the variation in the size of collected WO_3 particles as a function of stand-by time. The particles size remained 10 nm up to an incubation time of 24 h, after which it increased exponentially with stand-by time. From Figs. 3 and 4, it is considered that WO_3 particles are mainly monoclinic mixed with other structures, possibly orthorhombic or tetragonal structures, for the incubation period, then grow rapidly transforming to monoclinic structure.

3.2. Electrodeposited nanocrystalline Ni-WO_3

Fig. 5 shows the volume fraction of WO_3 in the electrodeposit as a function of Na_2WO_4-$2H_2O$ in the electrolyte. The volume fraction of WO_3 was estimated by assuming that the entire W detected by EDS was embedded as WO_3 particles, with no solute W. The volume fraction of WO_3 reached 6%; even at such a small volume fraction, the particles can strengthen the matrix by serving as obstacles to dislocations as in particle shear or the Orowan-type dislocation by-pass mechanism.

The grain size of the Ni matrix was determined by TEM. It is plotted as a function of Na_2WO_4-$2H_2O$ content of the electrolyte (Fig. 6). The average grain size slightly decreased to 16 nm with the addition of 40 and 60 g/L of Na_2WO_4-$2H_2O$. Then, it increased with increasing