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Effect of annealing on mechanical properties of nickel electrodeposited using supercritical CO_2 emulsion evaluated by micro-compression test

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ABSTRACT

Nanocrystalline nickel film was electrodeposited with supercritical CO_2 emulsion. The effects of annealing on nanocrystalline nickel were evaluated with scanning electron microscopy. The deposited films had a grain size of 16 nm with 2 at.% of interstitial carbon. A slight grain growth to 30 nm grain size was observed after low temperature (<200 °C) annealing. Higher temperature (>300 °C) annealing caused Ni_3C precipitation at grain boundaries and prominent grain growth above 300 nm grain size. Micro-compression samples of each annealed films and as-deposited film were fabricated to investigate the mechanical properties. Low temperature annealed nickel was fractured by cracking with higher yield strength compared to the as-deposited nickel while high temperature annealed nickel simply had a decrease in strength. The brittle fracture after annealing is suggested to be related to the redistribution of carbon and relaxation of grain boundaries. High yield strength of 1 GPa after 400 °C annealing is achieved thanks to the fine precipitates of Ni_3C.

1. Introduction

Electroplating is a key technology for fabrication of micro-components used in micro-electro-mechanical systems (MEMS). To obtain outstanding mechanical properties of the plated metal, we have developed an electroplating technique with supercritical CO_2 emulsion (EP-SCE) [1]. Supercritical CO_2 bubbles flowing in the electrolyte would bounce on the surface of cathode which removes hydrogen bubbles. The area in touch with CO_2 bubbles would be absence of electrolyte and the electrodeposition reaction is stopped then the reaction restarts when bubbles bounce away. Intermittent electrodeposition reaction known as periodic plating characteristics [2] gives grain refinement due to grain nucleation enhancement by interrupting the grain growth. The smallest grain size obtained was 8 nm with equi-axial grains [3].

Nanocrystalline materials with a grain size less than several tens of nanometer were extensively studied for its superior mechanical properties and unique thermal or mechanical response [4]. Although many mechanisms have been proposed to explain such behavior such as dislocation emission from grain boundaries [5,6], grain boundary sliding [7], and grain rotation [8], comprehensive work is still needed to determine what mechanisms dominate the nature of nanocrystalline materials. In one of our previous researches on nanocrystalline nickel produced by EP-SCE, we reported suppression of grain boundary mediated deformation due to dissolved carbon [9].

Thermal response on the mechanical properties has great interest for the actual use of electrodeposited metals as MEMS components, as well as studying unique phenomenon of nanocrystalline materials such as high thermal stability [10,11] and hardening by annealing [12–14]. MEMS components could be exposed to high temperature environment in soldering or in use. In this study, we investigate microstructural changes and changes in the mechanical properties in the films annealed at different temperature.

2. Experimental

2.1. Material fabrication

Nanocrystalline nickel fabrication by EP-SCE was well documented in previous papers [2,3]. In short, additive-free Watts bath with a nonionic surfactant, polyoxyethylene lauryl ether ($C_{12}H_{25}(OCH_2CH_2)_{15}OH$) was agitated with supercritical CO_2 to form emulsion. Electrodeposition was conducted on a pre-treated copper substrate for 3 h with constant current density of 2 A/dm^2 at temperature of 50 °C. The copper substrate was removed by mechanical cutting and polishing to isolate the 70 μm thick deposited nickel film. A following thermal treatment was

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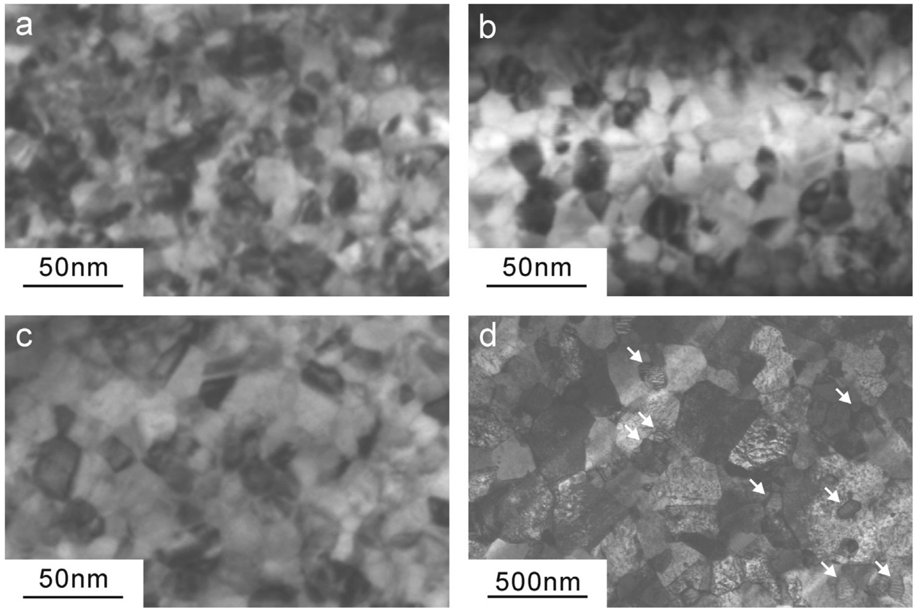

Fig. 1. Plane view STEM images of nickel films (a) as-deposited, (b) 150 °C annealed, (c) 200 °C annealed, (d) 300 °C annealed. White arrows in (d) indicate Ni_3C precipitates.

conducted in a vacuum at different temperatures from 150 °C to 400 °C for 2 h. For structural characterization, samples were thinned down to less than 100 nm thickness for electron transparency by using focused ion beam (FIB: FB2000A, HITACHI). Scanning transmission electron microscopy (STEM) observation was performed by scanning electron microscope (SEM: Ultra Plus, Zeiss) operated at 30 kV in bright field mode. Transmission Kikuchi diffraction (TKD) was acquired on the SEM equipped with Bruker e-Flash detector and analyzed by Bruker ESPRIT microanalysis software to obtain orientation maps and grain size.

2.2. Micro-compression test

Square pillars with side length of 20 μm and 40 μm in height were fabricated using FIB by vertical milling process [15]. Rectangular pillars milled out from edges of thin nickel films by using irradiation from thickness direction and further milling was conducted in $\pm 45°$ with respect to the film surface to access all faces of the pillar. Finally, each side of the pillar was milled at a glancing angle with 400 pA ion beam to minimize ion bombardment damage. The micro-compression of the pillar was conducted with a test machine specially designed for micro-sized materials by our group, more details can be found elsewhere [9,15]. Flat ended diamond indenter equipped to a load cell was displacement controlled by using a piezo-electric actuator. Loading was conducted at a constant displacement rate of 0.1 μm/s. The deformed pillars were observed by SEM.

3. Results and discussions

3.1. Microstructure

Fig. 1 shows STEM images of the nickel films. The as-deposited nickel had equi-axial 16 nm grain size as manually measured as the projection areas of more than 100 grains from several STEM images viewed from different directions. After low temperature annealing at 150 °C and 200 °C, a slight increase of grain size to 30 nm was observed. In nanocrystalline pure metals, abnormal grain growth often occurred at relatively low temperatures. Klement et.al [16] reported thermal instability of pure nickel initiated at 353 K as abnormal grain growth. In our nanocrystalline nickel, grain size distribution was small and equi-axial grains were observed. As reported in our previous paper, 2.6 at.% of carbon found in nickel film electrodeposited with EP-SCE by using glow discharge optical emission spectroscopy [17] which may be incorporated by reduction of CO_2 [18]. Supersaturated carbon easily segregated to the grain boundaries and caused solute drag which improves thermal stability of microstructure.

TKD analysis, also known as transmission electron backscattered diffraction analysis was conducted to obtain orientation and phase maps after phase identification using Kikuchi pattern. Using transmitted electron diffraction, travel distance of electrons inside the material is minimized and better spatial resolution could be obtained compared to the conventional EBSD measurement in tilted geometry [19]. Kikuchi pattern measurements was conducted at steps of 6 nm on the sample

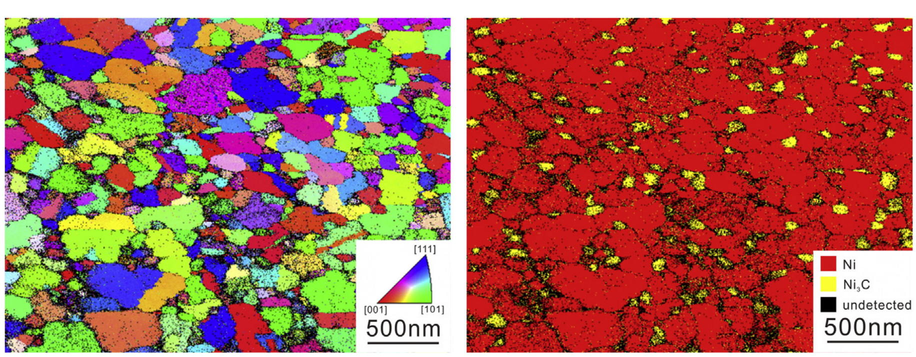

Fig. 2. (a) Orientation map and (b) phase map of nickel film annealed at 300 °C obtained from TKD analysis.