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Defect Structure in Electrodeposited Nanocrystalline Ni Layers with Different Mo Concentrations

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Abstract. The effect of molybdenum (Mo) alloying on the lattice defect structure in electrodeposited nanocrystalline nickel (Ni) films was studied. The electrodeposited layers were prepared on copper substrate at room temperature, with a constant current density and pH value. The chemical composition of these layers was determined by EDS. In addition, X-ray diffraction line profile analysis was carried out to study the microstructural parameters such as the crystallite size, the dislocation density and the stacking fault probability. It was found that the higher Mo content yielded more than one order of magnitude larger dislocation density while the crystallite size was only slightly smaller. In addition, the twin boundary formation activity during deposition increased with increasing Mo concentration. The results obtained on electrodeposited layers were compared with previous research carried out on bulk nanocrystalline Ni-Mo materials with similar compositions but processed by severe plastic deformation.

INTRODUCTION

Ni-Mo alloys are interesting materials with valuable properties, which endorse their applications in wide range of areas. Apart from the mechanical and thermal stability, they exhibit high hardness, wear and corrosion resistance. These substantial characteristics make them suitable for applications as hard coating materials [1] and also as substrate materials for superconducting coatings [2]. Nanocrystalline electrodeposited Ni-Mo thin films are potentially applicable as novel catalytic materials with ferromagnetism [3]. Moreover, Ni-Mo alloys have potential to serve as ecological alternatives to chromium plating in the automotive and decorative plating industry [4]. The electrodeposited Ni-Mo alloys can be used as an electrode for water splitting application. The high activity and long-term stability of nanocrystalline Ni-Mo facilitates their electro-catalytic application in hydrogen evolution reactions [5,6]. The strength and stability of nanocrystalline materials are important features for their efficient utilization. Therefore, the improvement of the mechanical strength of Ni-Mo alloys is vital for their aforementioned practical applications.

Nanocrystalline materials are known for their considerably improved properties compared to their conventional coarse-grained polycrystalline counterparts. The two main routes for the synthesis of nanomaterials are the bottom-up and the top-down approaches [7].

In this paper, the effect of Mo concentration on lattice defect structure of electrodeposited Ni layers was studied. For this purpose, two alloys with low and high Mo concentrations were prepared by electrodeposition on copper substrate. A comparative study for samples processed by both top-down and bottom-up techniques was also conducted. In a previous investigation, the severely plastically deformed Ni-Mo disks with similar compositions were processed by high pressure torsion (HPT) technique [8]. The results of this former research were compared with our present study, to gain deeper understanding of the influence of Mo addition on defect structure of Ni alloys processed by different techniques.

EXPERIMENTAL: MATERIALS AND PROCEDURES

Processing of Nanocrystalline Ni-Mo Layers

Electrodeposited Ni-Mo samples were prepared at room temperature with a galvanostatic electrolysis by using a solution containing 0.5 mol/liter NiSO₄, 0.26 mol/liter sodium citrate, 0.1 g/liter sodium dodecylsulfate as wetting agent, and Na₂MoO₄ in varying concentration up to 6 mmol/liter. It was particularly important to use a high-purity nickel sulfate salt with $c(\text{Co}) < 50$ ppm (produced by Jenapharm) in order to minimize the impurity content of the deposit. The bath was operated at $\text{pH} = 6.1 \pm 0.08$ where the deposition efficiency of pure Ni showed the maximum (about 98%) in a wide current density interval. The current density was -5.6 mA/cm^2 where the desired concentration range of Mo in the deposit could be achieved by varying the Mo content of the solution only and also the deposits were free of cracks by visual observation. The Faradaic efficiency was nearly constant, exhibiting a similar value as observed in the deposition of pure Ni. The substrate was a Cu sheet that was degreased prior to the deposition experiment and then placed horizontally at the bottom of the cell, allowing only the upward-facing side to contact the bath. A nickel wire spiral served as the counter electrode. The desired thickness of about 20 micrometer was regulated by the deposition time.

The chemical compositions of the electrodeposited layers were determined by energy dispersive spectroscopy (EDS) in a scanning electron microscope (SEM) and the results are listed in Table 1. The Mo contents in the layers with low and high Mo contents were 0.6 and 4.3 at%, respectively. Hereafter, the materials with low and high Mo concentrations are designated as ED-LMo and ED-HMo, respectively.

Characterization of Microstructure by X-ray Diffraction Line Profile Analysis

The microstructure of the Ni-Mo layers with low and high Mo concentration was investigated by X-ray line profile analysis (XLPA) using a high-resolution diffractometer (Rigaku) with $\text{CuK}\alpha_1$ radiation (wavelength: $\lambda = 0.15406 \text{ nm}$). The Debye-Scherrer diffraction rings were detected by two-dimensional imaging plates and XLPA was carried out by the Convolutional Multiple Whole Profile (CMWP) fitting procedure [9]. The instrumental broadening was negligible, compared to the physical peak broadening due to the nanocrystalline microstructure of the samples and therefore an instrumental correction was not taken into account. As an example, Fig. 1(a) shows the CMWP fitting for ED-LMo alloy. The open circles and the solid line indicate the measured and fitted patterns, respectively. The microstructural parameters including the area-weighted mean crystallite size ($\langle x \rangle_{\text{area}}$), the dislocation density and the twin fault probability were determined using this method. The area-weighted mean crystallite size was obtained using the equation $\langle x \rangle_{\text{area}} = m \cdot \exp(2.5\sigma^2)$, where m is the median and σ^2 is the log-normal variance of the crystallite size distribution. The twin fault probability in face-centered-cubic (fcc) materials is defined as the relative fraction of twin boundaries among the $\{111\}$ lattice planes.

RESULTS AND DISCUSSION

X-ray diffraction experiments revealed that the electrodeposited Ni-Mo films have a single-phase fcc structure (Fig. 1(a)). Although some peaks from the copper substrate were detected but no additional phase was present in the deposit. Strong (200) texture was observed for sample ED-LMo which was weakened with increasing Mo concentration (in sample ED-HMo). The crystallite size, the dislocation density and the twin fault probability values obtained by XLPA are listed in Table 1. According to Table 1, the crystallite size values for the two Ni-Mo layers were 40-50 nm, and the considerably higher Mo content yielded only a slightly smaller crystallite size. At the same time, Table 1 and Fig. 1(b) show that the dislocation density in sample ED-HMo is much higher ($\sim 173 \times 10^{14} \text{ m}^{-2}$) than that for ED-LMo film ($7 \times 10^{14} \text{ m}^{-2}$). Similarly to the dislocation density, the twin fault probability in ED-HMo layer is also larger by a factor of ~ 24 than in sample ED-LMo. These results indicate that the defect density in Ni-Mo films is very sensitive to the Mo content. The microstructures of the present electrodeposited layers are compared with bulk nanocrystalline Ni-Mo samples processed by the combination of two severe plastic deformation (SPD) techniques, namely cryorolling at liquid nitrogen temperature and an additional 20 turns of HPT at room temperature [8]. Table 1 shows the Mo content and the parameters of the microstructure for the two SPD-processed alloys which have similar Mo concentrations as the present electrodeposited films. The microstructural parameters correspond to the saturation state achievable by HPT method. It can be seen that similarly to the electrodeposited films, the SPD-processed samples with very different Mo contents have only slightly different crystallite sizes while the Mo

concentration has a very strong effect on the dislocation density, i.e., the higher Mo content yielded higher dislocation density. It should be noted, however, that this difference in the dislocation densities is not so high as in the case of the electrodeposited films. In addition, in the SPD-processed samples twin faults were not detected, irrespectively of the Mo concentration (see Table 1).

TABLE 1. Chemical composition of the nanocrystalline electrodeposited Ni-Mo alloys determined by EDS and the parameters of the microstructure obtained by XPLA. For comparison, the data determined for nanocrystalline Ni-Mo alloys processed by high pressure torsion (HPT) are also shown (the data were taken from [8]).

Ni-Mo sample	Mo content (at. %)	Crystallite size (nm)	Dislocation density (10^{14} m^{-2})	Twin fault probability (%)
ED-LMo	0.6 ± 0.1	53 ± 6	7 ± 1	0.2 ± 0.1
ED-HMo	4.3 ± 0.1	37 ± 4	173 ± 18	4.7 ± 0.5
Low-Mo (20 turns of HPT)	0.3 ± 0.1	40 ± 4	30 ± 3	0.0 ± 0.1
High-Mo (20 turns of HPT)	5.0 ± 0.1	30 ± 3	60 ± 6	0.0 ± 0.1

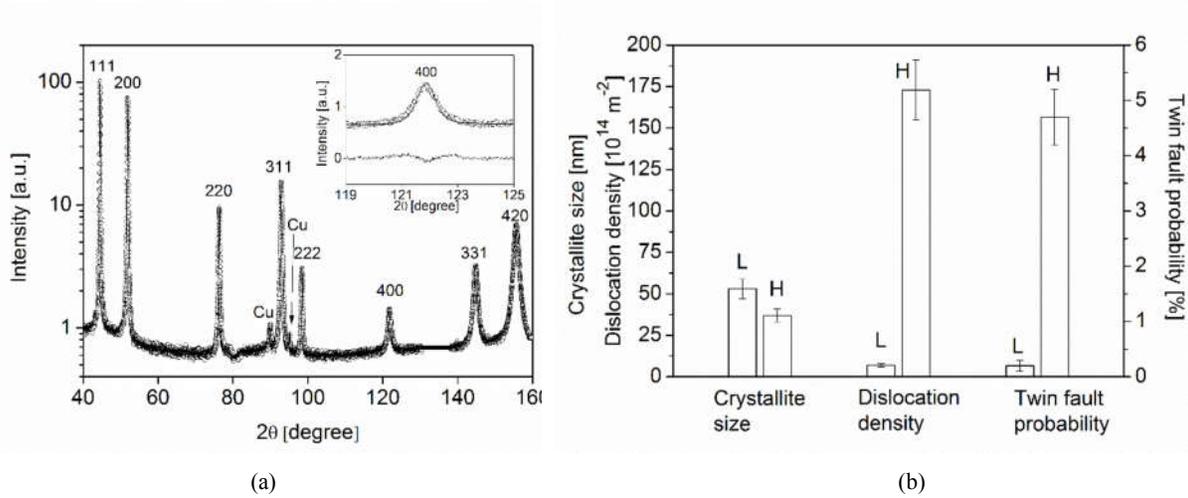


FIGURE 1. a) CMWP fitting of the X-ray diffraction pattern with logarithmic intensity scale for ED-LMo layer. The open circles and the solid line represent the measured data and the fitted curve, respectively. The inset displays a magnified part of the diffractogram in a linear intensity scale where the difference between the measured and the fitted patterns is also given at the bottom of the image. b) Histogram of the crystallite size, dislocation density, and twin fault probability in electrodeposited films with low (L) and high (H) Mo concentrations.

The origin of defects in electrodeposited and SPD-processed nanocrystalline Ni-Mo alloys is different. In the latter case, the dislocations developed due to the severe plastic straining. However, since many dislocations with opposite signs were formed, they could be annihilated by dynamic recovery processes during SPD, resulting in a saturation of the dislocation density. This saturation value depends on the melting point of the base material (Ni) and the solute content, since recovery is controlled by thermally activated diffusion [7]. The higher Mo concentration retarded the annihilation of dislocations, leading to a higher saturation dislocation density. In the case of the electrodeposited films, the lattice defects were formed in order to reduce the mismatch stress between the neighboring grains with different orientations. Therefore, the dislocations are growth defects and not caused by plastic deformation. Thus, the lattice defect structure is controlled rather by the deposition conditions [10] and not by the properties of the base material (e.g., melting point and stacking fault energy). Indeed, in SPD-processed Ni-Mo alloys twin faults were not detected, due to the high twin fault energy of Ni compared to other fcc metals. At the same time, in the electrodeposited films a significant twin fault probability was observed even for low Mo concentration. In fcc metals, twin boundaries have the lowest energy among the grain boundaries, therefore their formation during deposition is preferred. The size of Mo atoms is much larger than that for Ni atoms; therefore, their addition to Ni most probably increases the internal

stress in the as-deposited films. As a consequence, both dislocations and twin faults have higher densities for sample ED-HMo than in the case of layer ED-LMo. It can be concluded that although the increase of Mo content in nanocrystalline Ni increases the lattice defect density irrespectively of the processing technique, the strength of this effect depends on the production method.

SUMMARY AND CONCLUSIONS

1. Electrodeposited Ni-Mo layers with varying amount of Mo were prepared at room temperature under the conditions of fixed current density (-5.6 mA/cm^2) and pH of the electrolyte (~ 6.1). XLPAs investigations revealed that the increase of the Mo content from 0.6 to 4.3% yielded an increment in the dislocation density from $\sim 7 \times 10^{14} \text{ m}^{-2}$ to $\sim 173 \times 10^{14} \text{ m}^{-2}$. At the same time, the crystallite size was reduced only slightly from $\sim 53 \text{ nm}$ to $\sim 37 \text{ nm}$.
2. Similar change of the chemical composition in nanocrystalline Ni-Mo alloys processed by a top-down procedure (HPT), led to a smaller change in the dislocation density. Our results suggest that the microstructure in electrodeposited Ni layers is more sensitive to the Mo concentration than in the case of bulk Ni-Mo materials processed by severe plastic deformation. This is a consequence of the different roles of lattice defects in the development mode of the microstructure built up from nanocrystal entities.
3. The twin fault probability was practically zero in the SPD processed UFG Ni-Mo alloys due to the high twin fault energy of Ni, irrespectively of their Mo concentrations up to 5 at.%. At the same time, considerable twinning was observed in the electrodeposited films. With increasing the Mo content from 0.6 to 4.3%, the twin fault probability increased from 0.2 to 4.7%. This observation also indicates the high sensitivity of the defect structure to the Mo concentration in electrodeposited Ni.

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