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Crystallographic orientations and twinning of electrodeposited nickel—a study with complementary characterization methods

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ABSTRACT

A series of nickel layers was electrodeposited at different current densities from a Watts type electrolyte containing the additive 2-butyne-1,4-diol in various concentrations. The internal structure of the nickel electrodeposits was systematically investigated applying complementary microscopic and diffraction based characterization methods involving both surface and cross section investigations with different resolution and statistics. The complementary information gathered from combining the various techniques of microstructure characterization, in particular, supported the investigation of twins and the preferred crystallographic orientations of grains in the electrodeposits. Additive-free deposition results in relatively large columnar grains with numerous growth twins of nanoscale dimensions. The presence of the additive in the electrolyte yields considerable grain refinement already at low additive concentration, but the preferred crystallographic orientation of grains changes gradually with increasing additive concentration and twins with nanoscale dimensions are detected also in these samples.

1. Introduction

For nickel layers, electrodeposition from the Watts electrolyte [1] certainly is most popular and has been extensively used, both for decorative purposes and the synthesis of functional electrodeposits. The Watts electrolyte with the basic composition of nickel sulfate, nickel chloride and boric acid originally does not contain additives. Modifications by the addition of various organic additives were developed for tailoring microstructure and properties of electrodeposited nickel dedicated to specific applications. One of the most common additives for the Watts electrolyte is 2-butyne-1,4-diol (hereafter BD). This relatively simple molecule, which neither contains nitrogen nor sulphur, is a powerful class(II) brightener with the ability of both brightening and levelling during the electrodeposition of nickel [2–5]. The long standing experiences of applying BD in a Watts-type electrolyte are numerously reported in the literature comprising both its chemical nature and the effect on altering the internal structure of the nickel electrodeposits (e.g. [6–9]). One of the major results of previous studies, although this partly dates back some decades, is the collection of data on crystallographic texture in diagrams showing the occurrence of a certain texture and the transition between different texture components as a function of typical parameters (like pH-value, current density or additive concentration) of the electrodeposition process [3,5]. As a function of the applied process parameters, various preferred grain orientations yielding fiber textures of <111>, <110>, <100>, <211>, <210> or combinations thereof are frequently observed for electrodeposited nickel [3,5,7,10]. Recently, on the example of copper electrodeposits, the importance of twin boundaries, i.e. special boundaries between grains comprising a well-defined crystallographic orientation relation, has been documented [11,12]. The twin boundaries allow the unique combination of strength and ductility for copper electrodeposits and, in addition, enhance the (thermal) stability of the as-deposited layers [11]. Thus, twins also are of interest for the mechanical properties of nickel layers. Consequently, for microstructure analysis of nickel electrodeposits, not only the main texture components representing the majority of grain orientations, but, in addition, possible (minor) twin orientations and the corresponding detection of twins in the microstructure become of interest. Material synthesis must be closely linked to advanced microstructure analysis with particular focus on the crystallographic orientation of grains, corresponding misorientations and the characteristics of the grain boundaries [13]. In this respect, not only layers obtained from dedicated electrochemical deposition applying novel electrolytes or refined operating conditions, but also rather conventional layers deposited from well-established electrolytes are of interest for detailed microstructure characterization with advanced methodology.

The present work reports about the internal structure of nickel electrodeposited from a Watts type electrolyte. Cross sections covering the whole layer thickness from the substrate to the surface were systematically investigated by the complementary use of microscopy and

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diffraction techniques with particular focus on the crystallographic orientation of grains as a function of the applied deposition conditions.

2. Experimental

2.1. Electrodeposition

Electrochemical deposition of nickel layers was carried out from a Watts-type bath with the following basic chemical composition: 300 g dm^{-3} nickel sulfate $NiSO_4 \cdot 7H_2O$, 35 g dm^{-3} nickel chloride $NiCl_2 \cdot 6H_2O$, 40 g dm^{-3} boric acid H_3BO_3. The electrolyte was used either without any organic additive or after adding 2-butyne-1,4-diol (BD) in concentrations of 5, 10 and 15 mMol dm^{-3}. For each of the mentioned electrolyte compositions, samples were deposited at three different current densities: 2, 5 and 10 A dm^{-2}, which yields 12 different samples (see Table 1). Samples are referred to names that indicate the values of applied additive concentration and the current density. For example, sample A5-C10 was deposited from an electrolyte containing 5 mMol dm^{-3} of the additive BD using a current density of 10 A dm^{-2}.

The electrolyte with a pH value of 4.5 was kept at a constant temperature of 50 °C and mechanically stirred during deposition. Since the deposition rate strongly depends on the applied current density, the deposition time was chosen in relation to the current density such that identical charge transfer was achieved for all samples. Variations of the resulting layer thicknesses (between 10 μm and 19 μm) indicate differences in the current efficiency during growth of the various nickel deposits.

Pure copper sheets were used as working electrodes, which prior to nickel deposition were subjected to electroless plating of nickel–phosphorus (Ni–P) from a commercially available electrolyte (NIPOSIT™ 65R) for deposition of a several micrometer thick amorphous Ni–P layer. A total area of (50 × 43) mm^2 was deposited on each substrate, from which small pieces were cut for microscopic analysis. The purpose of the amorphous Ni–P layer is avoiding any crystallographic orientation relation of the growing electrodeposit with the crystalline Cu substrate.

2.2. X-ray diffraction

The electrodeposited nickel layers were investigated with X-ray diffraction, XRD, for quantitative crystallographic texture analysis and line profile analysis. A D8 Discover X-ray diffractometer from Bruker AXS equipped with an Eulerian cradle was applied and operated with Cu-Kα radiation.

For quantitative texture analysis, pole figures of 111, 200 and 220 reflections were measured applying sample rotations around the surface normal. The azimuth angle φ was varied in the range of $0 \leq \varphi \leq 360°$ at a step size of 5°; the sample tilts, i.e. the pole angle ψ, was varied in the range of $0 \leq \psi \leq 75°$ at a step size of 5°. Measured intensities were corrected for background and a Ni-powder standard was used for defocusing correction. For texture quantification, the orientation distribution function was calculated. As ideal fiber textures apply for all nickel electrodeposits, maxima in the inverse pole figures in normal direction to the substrate were used to determine the fiber axis <uvw>. Inverse pole figures in directions within the plane of the deposit represent random rotations around the fiber axis. Accordingly, the corresponding orientation densities in the normal direction are a measure of the texture strength.

XRD line profile analysis was carried out to determine the crystallite size (size of coherently diffracting domains) and the microstrain for the nickel layers. Several reflections corresponding to 111, 200, 220, 311, 222, 400, 331 and 420 diffracting lattice planes of nickel were measured applying a step size of 0.02°2Θ. The measured line profiles were fitted with a superposition of two pseudo-Voigt functions, corresponding to the Kα_1- and the Kα_2-components, which yielded the position, width and shape as well as the integrated intensity of the individual reflections. Only parameters corresponding to the Kα_1-component were used for further evaluation. After correction of the measured line widths for the effect of instrumental broadening applying a standard powder sample composed of LaB_6, the resulting physical broadening of the diffraction lines was evaluated with the classical Williamson-Hall analysis [14].

Table 1
Nickel layers electrodeposited at various current densities from a Watts-type bath containing different levels of the additive 2-butyne-1,4-diol (BD).

BD concentration/mMol dm^{-3}	Applied current density, j/A dm^{-2}		
	2	5	10
15	A15-C2	A15-C5	A15-C10
10	A10-C2	A10-C5	A10-C10
5	A5-C2	A5-C5	A5-C10
0	A0-C2	A0-C5	A0-C10

2.3. Electron and ion beam microscopy

A dual beam microscope, Helios Nanolab™ 600 from FEI, combining a field emission gun scanning electron microscope (SEM) and a focused ion beam (FIB) was used both for ion channeling contrast imaging (ICCI) of the microstructure and for electron backscatter diffraction (EBSD) analysis.

For cross section preparation, a piece cut from the deposited sample was clamped in-between two brass plates with an aluminium foil protecting the surface of the nickel layer. This sample holder was used for cross section preparation by means of manual grinding on SiC paper of grade 1000 and 4000, followed by mechanical polishing applying a 3 μm and 1 μm diamond suspension and mechanical–chemical polishing with 0.04 μm colloidal silica (OPS from Struers). FIB capabilities were also applied for the final preparation of the mechanically prepared cross sections for EBSD analysis. For this purpose, ion beam milling with 30 keV Ga$^+$ ions was carried out in the dual beam microscope in two steps: First, about 700 nm of the mechanically prepared surface was removed applying a current of the ion beam of 2.8 nA, followed by gentle milling with an ion current of 0.46 nA for removal of another 50 nm. Smooth and artifact free surfaces were obtained by this procedure.

EBSD analysis covering the whole cross section of the nickel electrodeposits was obtained using an EBSD mapping system (TexSEM Laboratories, Inc.) and a high speed Hikari EBSD detector. The SEM was operated at an acceleration voltage of 12 kV and a probe current of 1.4 or 5.5 nA. For EBSD mapping, a step size of 25 nm was applied. Data evaluation was carried out applying the software OIM 5™ from EDAX, TSL.

The ion beam in the dual beam microscope was not only applied for milling, but also for imaging the microstructure of the electrodeposited nickel. The prepared cross sections were investigated by means of ICCI. For microstructure imaging, the FIB was operated at an acceleration voltage of 30 kV and the applied probe current was chosen such that the samples were exposed to the ion beam as gentle as possible. To this end, the applied probe current was optimized for each sample depending on the morphology of the nickel deposit (ion densities ranging from 0.6 to 3.4 C/m^2 were applied). ICCI was performed with particular care for minimizing possible ion beam induced changes of the microstructure and was always carried out as a final investigation, i.e. after EBSD had been carried out on exactly the same location of the sample.

The surface topography of all nickel electrodeposits was investigated in the SEM using secondary electron imaging without any sample preparation.

Transmission electron microscopy (TEM) was used for selected samples with nano-sized twin lamellae which were below the resolution limit of ICCI. Plane view preparation was carried out by electropolishing such that an electron transparent thin foil was obtained from a location