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Influence of Additives on Texture Development of Submicro- and Nanocrystalline Nickel

U. Klement[1,a], C. Oikonomou[1,b], R. Chulist[2,c], B. Beausir[2,d], L. Hollang[2,e] and W. Skrotzki[2,f]

[1]Materials and Manufacturing Technology, Chalmers University of Technology, SE-412 96 Gothenburg, Sweden
[2]Institut für Strukturphysik, Technische Universität Dresden, D-01062 Dresden, Germany

[a]uta.klement@chalmers.se, [b]chroik@chalmers.se, [c]robert.chulist@physik.tu-dresden.de, [d]benoit.beausir@univ-metz.fr, [e]hollang@physik.tu-dresden.de, [f]werner.skrotzki@physik.tu-dresden.de

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Abstract. Organic additives such as saccharin have been frequently used in electroplating operations to moderate deposit growth rates and to control film quality. In this study, texture development upon annealing of pulse-electroplated Nickel produced without additives is analyzed by use of electron backscatter diffraction technique.

Plating without additives results in a microstructure with slightly elongated grains and a <110> fibre texture in growth direction and this texture is conserved upon annealing up to 600°C. Structural units in form of groups of elongated grains possessing a common <110> zone axis in growth direction and twin relationships between themselves are found in the microstructure. For revealing the influence of additives, the observations are compared with results obtained for Ni and Ni-Fe plated in the presence of additives where during abnormal grain growth the initial <411> fibre texture changes to an energetically more favourable <111> texture by twinning. The lack of additives is assumed to be responsible for the observed differences in texture and microstructure development.

Introduction

Electrodeposition is an advanced synthesis technique which involves the creation of a coating or free-standing material through an electrolytic process. The microstructure and texture of the final product and subsequently its properties are affected by many parameters such as pH and temperature of the electrolyte, current density, and overvoltage. For obtaining a nanocrystalline material the electrolyte often contains stress reliever and grain refining agents. Organic additives such as saccharin have been frequently used in electroplating operations to moderate deposit growth rates and to control film quality. According to literature [1-3], the addition of saccharin leads to the formation of fine crystallites that have a preferred <111> orientation with the growth direction (GD). But also double fibre textures have been observed in Ni and Ni base alloys in the presence of additives: a <200> <111> double fibre texture was found for Ni with 10 and 20 nm grain size and a sulphur content of 1580 ppm S and 1200 ppm S, respectively [4], and a <411> <111> double fibre texture was observed by X-ray diffraction and electron backscatter diffraction (EBSD) measurements in Ni and Ni-Fe [5]. Upon annealing, the materials usually develop a strong <111> texture with respect to the growth direction [4-8]. Twinning was found to be one of the mechanisms responsible for the orientation change [5].

Ni electrodeposits produced from an additive-free bath may exhibit <110>, <100>, or <210> texture [3,9]. Amblard et al. [10] explained the occurrence of the different textures by different inhibitors as result of hydrogen co-deposition. Hence, the presence of additives and/or inhibitors is important for grain refinement but also plays a crucial role for the texture of electroplated materials. In this study, texture development upon annealing of pulse-electroplated (PED) Ni produced without additives is analyzed.

Experimental

Submicrocrystalline Ni was produced by PED technique without additives for grain refinement. The electrolyte was based on Ni-sulfamate stabilized with boric acid and the main deposition parameters are as follows: Bath temperature (65°C) and a pH value of 4.2 were kept constant during the deposition process; a pulse current of 2 A/dm^2 was chosen; pulse-on time t_{on} = 5 ms and pulse-off time t_{off} = 45 ms. Carbon and sulphur content of the electrodeposit were measured to be 110 and 80 ppm, respectively.

EBSD measurements were performed in a Zeiss Ultra 55 and a Leo 1550 Gemini field emission gun scanning electron microscope (SEM). Both instruments were equipped with HKL Channel 5 EBSD system and Nordlys detectors. Samples (both parallel and perpendicular to the GD of the electrodeposit) were prepared by mechanical grinding with SiC paper down to grit size 4000, followed by electropolishing using a Struers Lectropol-5 and an electrolyte consisting of sulphuric acid, acetic acid, distilled water at 10°C and 8V. Furnace annealing treatments were performed for 20 min at 350, 400, 450, 500, 550, and 600°C followed by air cooling.

Results and Discussion

Grain boundary maps parallel to GD of the as-prepared material and after annealing at 350 and 600°C are shown in Fig. 1. In the as-prepared state and perpendicular to GD, the grains are nearly equiaxed and have an average grain size of 100 nm (not shown). Parallel to GD, the average grain size is 170 nm as the microstructure consists of elongated grains in an equiaxed matrix (Fig. 1a). The size of the elongated grains increases with plating thickness. Hence, the electrodeposit is having a graded microstructure. This is not unusual for nickel electrodeposits. After annealing at 350 and 600°C, grains are grown and the microstructure parallel to GD is clearly bimodal. Using the line intercept method, the average size of the grains in GD is 210 nm at 350°C (Fig. 1b) while it is 125 nm perpendicular to GD. Between 350°C and 600°C, a rapid increase in the average grain size is noticed and at 600°C, the average grain size is 761 nm when measured parallel to GD (Fig. 1c), and 484 nm when measured perpendicular to GD.

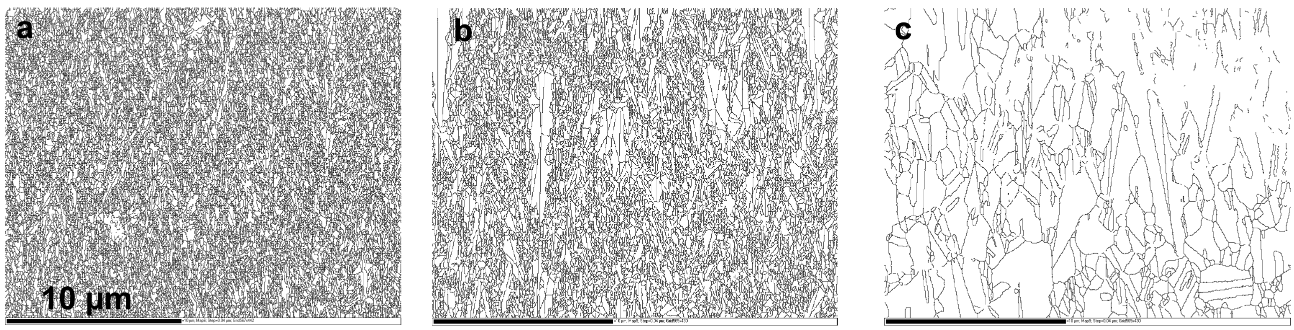

Fig. 1: EBSD grain boundary maps of PED nickel parallel to GD (vertical): (a) as-prepared state; (b) after annealing for 20 min at 350°C; (c) after annealing for 20 min at 600°C.

EBSD orientation maps revealed the presence of a <110>//GD fibre texture in the as-prepared state and after annealing. That means the texture is not changing upon annealing. Subsets of the orientation maps obtained after annealing at 350 and 600°C were created to examine the dominant <110>//GD texture (Fig. 2). The orientation maps are depicted with inverse pole figure (IPF) colour code with respect to the GD, and a minimum deviation angle of 15° is chosen. Twin boundaries are also included in the images. As can be seen in comparison with the grain boundary maps in Fig. 1, the <110>//GD oriented grains comprise all the elongated grains present in the microstructures. These grains grow predominantly in length upon annealing and dominate the microstructure and the texture at 600°C. The subsets in Fig. 2 also reveal that many of the <110>//GD grains are in twin orientation relationship to each other. The twin boundaries are parallel or only slightly inclined to the GD. The importance of these twin boundaries for the evolution of the microstructure and texture is best seen in a more detailed investigation of isolated grain groups.

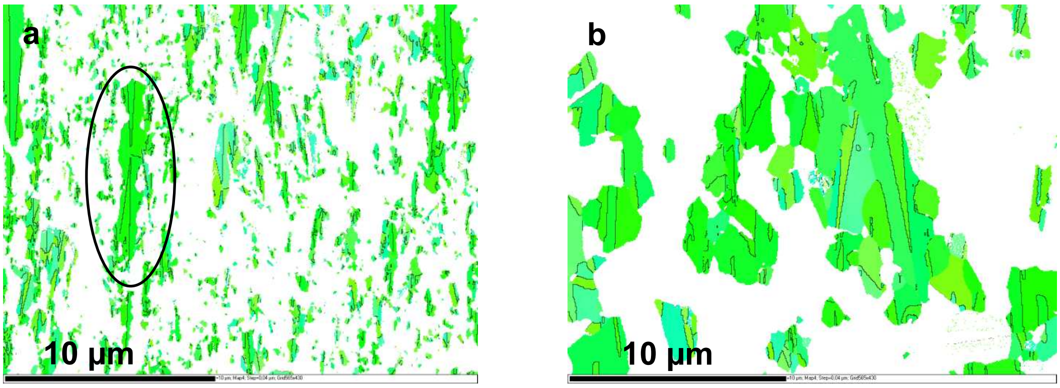

Fig. 2: Subsets of <110>//GD oriented grains (minimum deviation angle of 15°) from EBSD orientation maps of electrodeposits annealed for 20 min at (a) 350°C and (b) 600°C. Marked grain colony is analyzed in Figs. 3 and 4.

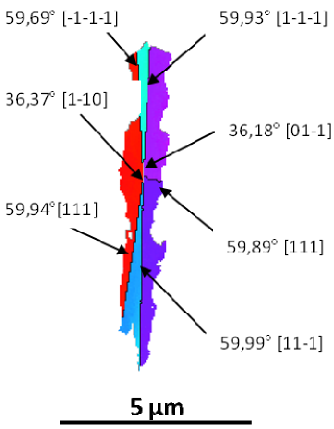

Fig. 3: Colony of grains from the orientation map obtained from the sample annealed for 20 min at 350C.

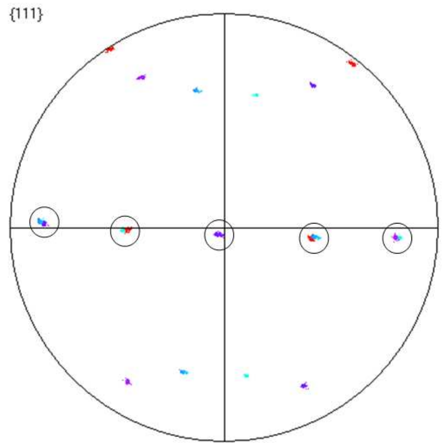

Fig. 4: <111> pole figure for the grains shown in Fig. 3. The twin poles are marked.

Figure 3 shows a colony of elongated grains that has been found after annealing at 350°C (marked in Fig. 2a). Notice, that the IPF colouring is chosen perpendicular to the GD; parallel to the GD all the grains have <110> orientation as seen in Fig. 2a. A distinct pattern is found for these grains: Between the five grains (in a circle) twin orientation relationships are established (measured orientation relationships are given in Fig. 3). As there is no junction where all grains are meeting, the orientation between the grain on the left (red) and the grains on the right (purple and dark blue) are of type Σ9 (38.9°<110>) considering Brandon's criterion. As can be seen in Fig. 4, the twin axes are all spread along the equator of the pole figure (marked by circles), indicating that the twin planes are all perpendicular to the GD. Five-fold symmetries (<110>//GD oriented grains with common zone axis) were also observed when investigating the electrodeposit perpendicular to the GD. Hence, independent of the direction, parallel or perpendicular to GD, the same behaviour is seen for these grains. However, as in the example shown above (parallel to GD), the grains are usually not forming one junction in the centre. Instead, Σ9 boundaries are observed (already in as-prepared state). Five grains with 70.53°<110> orientation relationship to each other make almost a full circle (352.64° instead of 360°), while 60°<111> orientation relationships require 6 grains for achieving a full circle/identity. Hence, the generated stresses (associated with the deviation in rotation angle) are most likely the reason for the formation of Σ9 boundaries in the centre of the grain colonies. Evans [11] already showed that <110> oriented deposits are associated with higher values of internal stress as compared to electrodeposits with <100> texture. Despite stresses, the formation of these distinct structural units seems to be energetically favourable as they grow and dominate the microstructure upon annealing. Grains having a <110>//GD texture and forming twin relationships in-between them were also reported in previous studies. Also structural units with five-fold symmetry were observed and described before [9,12,13]. Like in our case, five grains possessing a common <110> zone axis (<110>//GD) are separated by twin boundaries. However, their measurements were only performed perpendicular to GD and in the as-prepared state. Hence, the 3D-structure (twin relations parallel and perpendicular to GD) of the structural units and their dominating role at elevated temperatures was not seen before.

Conclusion and Summary

The additive-free Ni electrodeposit investigated in this work contains elongated grains providing the material with a <110>//GD fibre texture in as-prepared state. This texture is conserved even at elevated temperatures (600°C). Structural units with stable twin configuration in combination with Σ9 boundaries parallel and perpendicular to GD are formed. This is a very different microstructure and texture development as observed in Ni electrodeposits produced in the presence of additives. In those materials, twinning is observed to form new, fast growing, low energy orientations dominating the final texture. In additive-free material, in contrast, twinning occurs for stabilizing the present configuration.

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