Characterization of multiple twinned structural units in pulse-electrodeposited nickel

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Abstract. The investigation was performed on pulse-electrodeposited Nickel with sub-microcrystalline microstructure containing slightly elongated grains having a <110> fibre texture in growth direction. Structural units in form of groups of elongated grains possessing a common <110>-zone axis in growth direction and CSL boundaries (in some cases twins) between them have been found in the microstructure by use of EBSD. Grain growth sets in above 325°C but the texture is conserved up to at least 600°C. This means that the arrangement of twins and other CSL boundaries stabilized the structural units; there is no orientation change (by further twinning) when grain growth occurs as seen in previous studies on Ni and Ni-Fe of different initial texture. The observed structural units were characterized in detail and the occurring grains and grain boundaries are described.

1. Introduction

Materials with nano- and sub-microcrystalline grain sizes have been intensively studied due to their potential in high strength applications and as wear resistant coatings. A common way to produce materials with such length scales is pulse-electrodeposition. Depending on the process parameters, the resulting grain size and texture can be tailored. For example, for Nickel electrodeposits produced from an additive-free sulfamate bath, <100>-, <110>- and <210>-textures were reported [1-3]. Texture formation is said to be governed by the adsorption of an inhibiting species, i.e. hydrogen [4]. The higher the adsorption on a specific crystallographic plane, the slower is its growth velocity. As a consequence, the growth in some crystallographic directions is faster than in others and a textured material is obtained.

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 [5-7], 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 and 1200 ppm, respectively [8], and a <411> <111> double fibre texture was observed in Ni and Ni-Fe electrodeposits by using X-ray diffraction and by performing measurements using electron backscatter diffraction (EBSD) technique [9]. Upon annealing, abnormal and normal grain growth sets in and the final <111> texture with respect to GD is obtained with one or two twinning operations from the initial texture of the as prepared material [8-12].

The presence of twins and other low-Σ boundaries (use of coincidence site lattice (CSL) description [13]) in the microstructure is known to significantly improve mechanical

properties (grain boundary engineering). Related to a high twin density, 5-fold twins have been observed for different materials [14-16]. However, also structural units including other low-Σ boundaries than twins have been reported [17,18]. Common to the grains in 5-fold twins and low-Σ structural units is a <110>-orientation parallel to GD. Moreover, investigations perpendicular to GD showed clearly the 3-dimensional character of structural units [17,18]. In this paper, these structural units are investigated in more detail both parallel and perpendicular to GD.

2. Experimental

Two different pulse-electrodeposited Nickel materials were investigated. One of which was produced at TU Dresden, Germany, the other one at the Indian Institute of Science (IISc) in Bangalore, India. The experimental procedure will be described elsewhere but in both cases a saccharine free sulfamate bath was used and the materials had a <110> fibre texture in GD. The material from Germany had slightly elongated grains in GD (aspect ratio of 1.8) and a grain size of about 180 nm. The Ni electrodeposit from India had an average grain size of 190 ± 100 nm. Both materials did not show noticeable grain growth when heat treated at temperatures below 325°C. To investigate thermal stability, differential scanning calorimetry (DSC) measurements were performed up to 823 K in argon atmosphere at a heating rate of 10 K/min.

EBSD measurements were performed in a Leo 1550 Gemini field emission gun scanning electron microscope (SEM). The instrument was equipped with a Channel 5 EBSD system by Oxford Instruments and Nordlys II detector. Samples oriented parallel as well as perpendicular to 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 A2 electrolyte consisting of perchloric acid, ethanol, 2-butoxyethanol and distilled water. In addition, samples were prepared by mechanical grinding and polishing. Grinding was performed on P2400 and P4000 sandpaper to achieve a flat surface. Afterwards, the sample was polished on MD-Nap with 6 µm, 3 µm and 1 µm diamond paste. Final polishing was performed with OPS on MD-Chem. Between the individual steps, the samples were carefully cleaned with ethanol. After the final polishing step, the samples were cleaned for 3 minutes in an ultrasonic bath containing isopropanol. Furnace annealing treatments were performed for 20 min at 350, 400, 450, 500, 550, and 600°C followed by air cooling.

3. Results and discussion

The DSC curve showed the typical shape of a nanocrystalline electrodeposits consisting of a low-energy exotherm and a main heat release peak. However, it is important to notice that for the investigated materials both the onset of the low-exotherm and the main heat release peak have higher values than the ones recorded for Ni samples with 20 nm grain size and <100><111> double fibre texture. In fact, the onset of the low-energy exotherm was at 325°C (material from Germany) instead of 84°C, while the heat release peak was with 395°C more than 100 degrees higher than in the Nickel material with 20 nm grain size (289°C) [19]. Hence, the Nickel material with <110> fibre texture has a higher thermal stability.

Figure 1 shows the EBSD orientation map in inverse pole figure colouring (coloured parallel to GD) of a Ni sample investigated perpendicular to GD (side view). The orientation map is superimposed to the band contrast image and the sample was heat treated for 20 min at 350°C. As can be seen, the microstructure consists of elongated grains arranged in structural units which all have a <110>-axis parallel to GD (grains are green according to inverse pole figure colour code). When investigating the grain boundaries within the structural units, mainly twin boundaries are found. However, due to the arrangement of the grains, Σ9 grain boundaries are observed in the centre of the structural units. Two examples encircled in Fig. 1 are shown in higher magnification in Fig. 2. Notice, that the structural units shown in Figs. 2

(c) and (d) are not showing a <110> fibre texture as they are not coloured in green. Nevertheless, the example may be a 5-fold twin (the same goes for the encircled structural unit at the lower left corner in Fig. 1). The presence of the Σ9 boundary in the centre (only 1 pixel between the blue grain at the top and the purple grain at the bottom; illustrated by an arrow in Fig. 2d) may be due to the resolution of the EBSD map. On the other hand, a 5-fold twin may be surprising since the twins are described by 60°<111> orientation relationships (6 grains with 60°<111> orientation relationship and common <111>-axis would be required for achieving a full circle/identity). However, the grains do not have a common <111>-axis as seen from the pole figure in Fig. 3. In fact, the grains have a common <110>-axis which is tilted out of the y-direction which is parallel to GD.

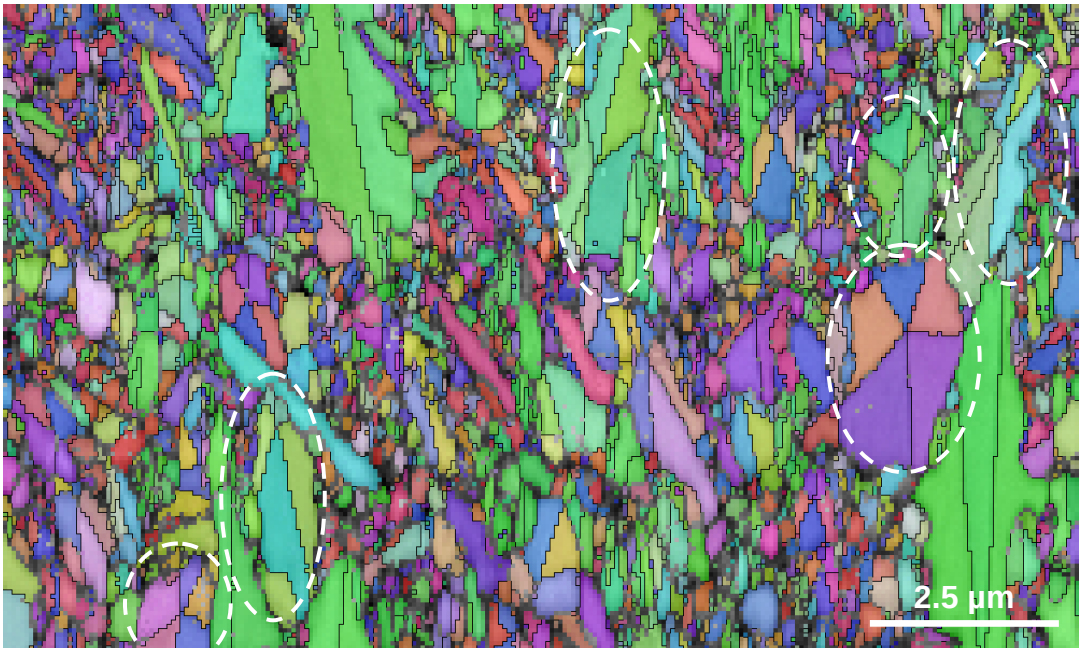

Fig. 1: Inverse pole figure superimposed on band contrast image of a Ni-sample investigated perpendicular to the GD (the colouring is chosen parallel to GD). Black lines illustrate large angle grain boundaries (rotation angle > 10°).

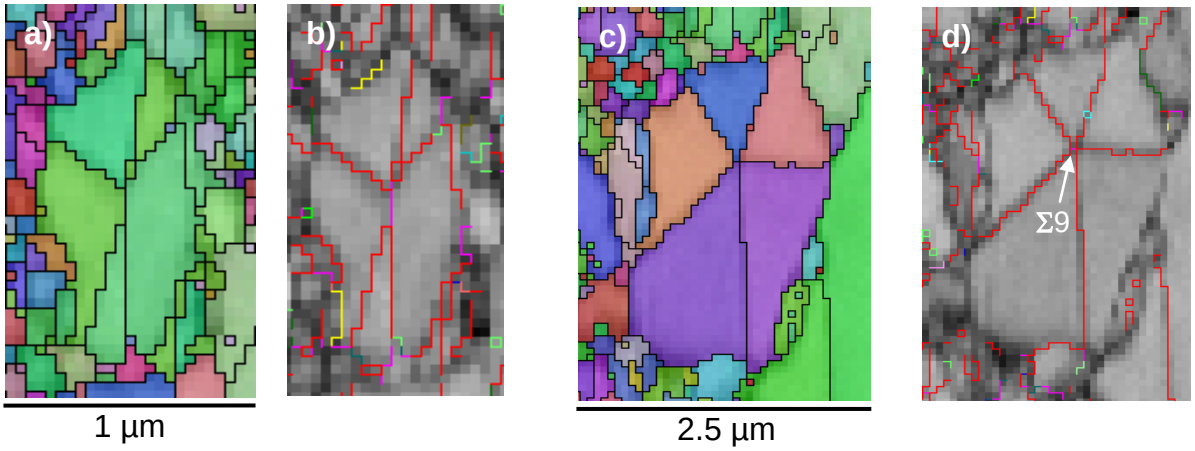

Fig 2: Magnified areas from Fig. 1 ((a) and (c)) and respective band contrast images ((b) and (d)) with Σ boundaries given in colour: Σ3: red, Σ9: pink, Σ11: yellow, Σ13a: light blue.

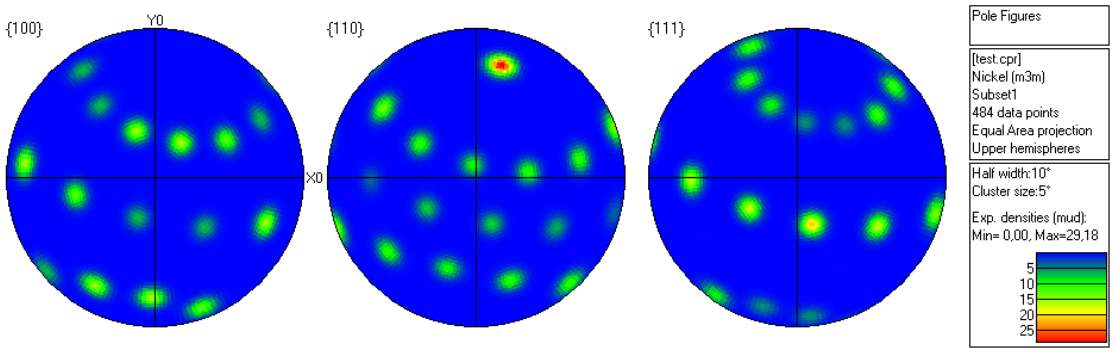

Fig. 3: Pole figures of the structural unit (subset of 5 grains) in Fig. 2 (c) (y-direction parallel GD).

As seen in the examples shown above (Fig. 1), the grains of structural units are usually not meeting in the centre, i.e. they are not forming a common junction. In Fig. 4, a structural unit obtained after heat treatment of 20 min at 500°C and measured perpendicular to GD (side view) is provided in higher magnification (the orientation map is coloured perpendicular to GD while a colouring parallel to GD is shown in the inset in the upper left corner). As can be seen, the hit rate at the centre of the structural unit is too low and no orientation information was obtained (only wild spikes are removed and no additional noise control in form of addressing orientations to zero solutions was performed). For identification of orientation relationships between the grains of the structural unit, the coincidence site lattice (CSL) concept and Brandon's criterion were used [13,20] and all grain boundaries could be identified as low-Σ boundaries, i.e. below Σ27 (Fig. 4 (b)). Solid lines represent grain boundaries that are clearly identified, while dotted lines indicate the position of assumed grain boundaries (not measured due to low local hit rate). Position and character of these grain boundaries were chosen in a way to not violate the combination rule [21]. Following this concept, the grains of the structural unit have twin boundaries between neighbouring grains while in the centre Σ9 and Σ27 grain boundaries (multiple twins) are assumed to be present.

When investigating structural units in top view, i.e. parallel to GD, 5 grains with twin orientation relationship to each other (70.53°<110>) make almost a full circle (352.64° instead of 360°). The missing 7.35° are supposed to be accommodated by internal elastic strain [22]. Figure 5 shows a structural unit in which one of the grains has an orientation gradient (up to 6°; best visible when coloured in y-direction) to accommodate for the low-Σ grain boundary arrangement. The orientation map is processed only slightly, i.e. wild spikes are removed and minor noise reduction is performed (6 nearest neighbours required). Consequently, there are still a large number of zero solutions (mainly at grain boundaries) where the measured patterns could not be identified unequivocally. In Fig. 6, position and character of the grain boundaries are provided which were obtained by taking into account Brandon's criterion and combination rule [20,21]. Again, solid lines are used to describe grain boundaries that are clearly identified by measurement, while dotted lines are used to indicate the position of assumed grain boundaries. As in the previous case, the structural unit can be described by low-Σ grain boundaries ($\Sigma \leq 33$).

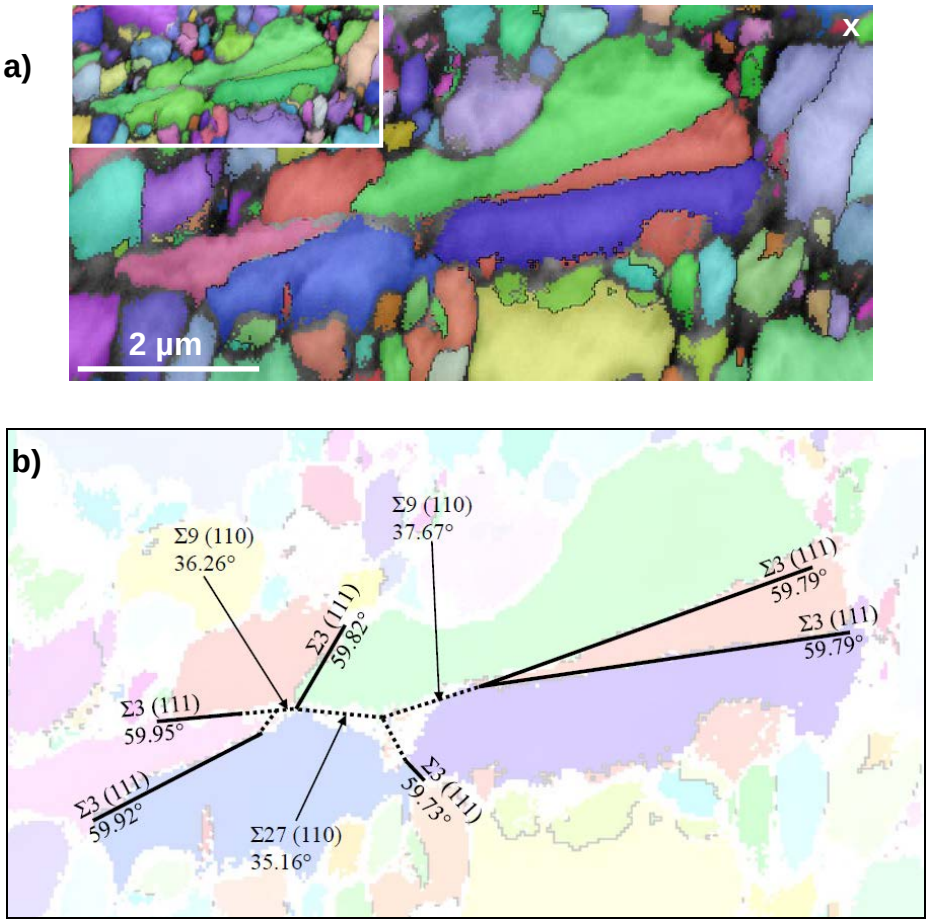

Fig. 4: (a) EBSD orientation map of structural unit in inverse pole figure colouring (chosen perpendicular to GD) superimposed on band contrast image after heat treatment for 20 min at 500 ℃. The inset (upper left corner) shows the orientation map coloured parallel to GD. (b) Illustration of the grain boundary arrangement in the structural unit seen in (a).

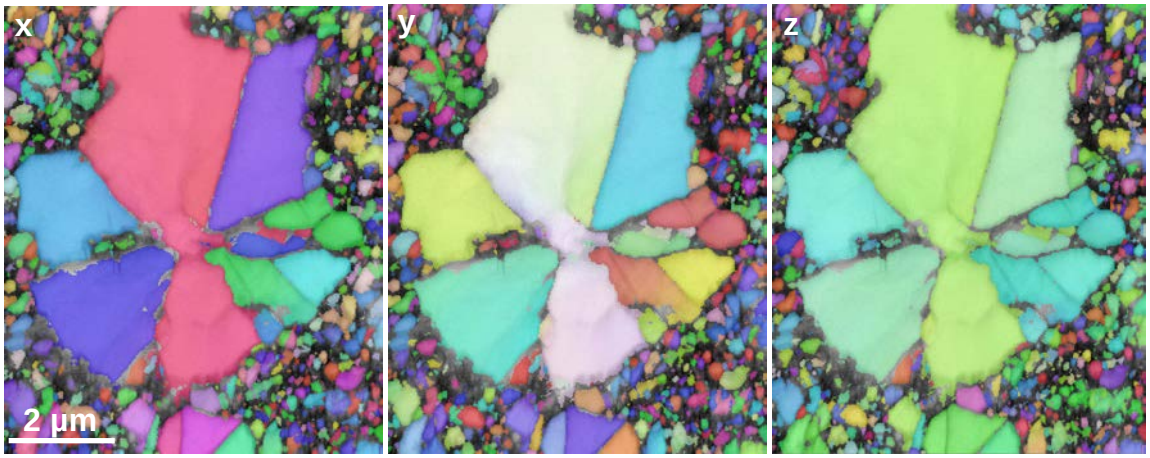

Fig. 5: EBSD orientation map in inverse pole figure colouring superimposed on band contrast image of a structural unit measured parallel to GD (z || GD).

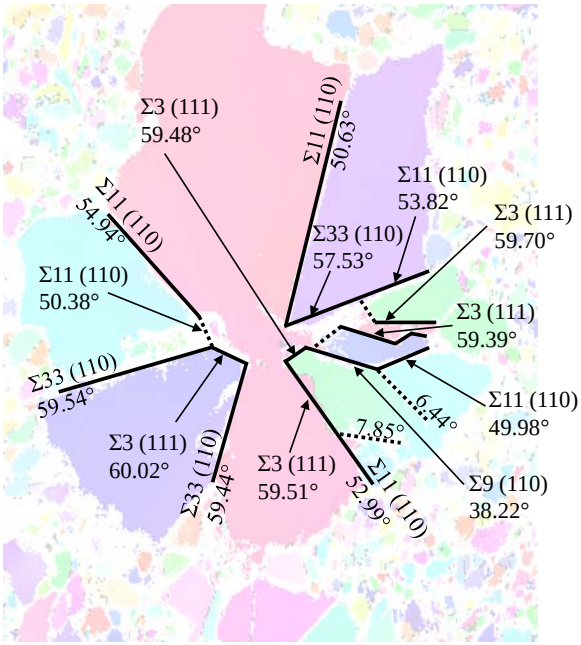

Fig. 6: Grain boundary arrangement of the structural unit in Fig. 5.

In the measurements parallel to GD, no 5-fold twin structure was observed. Instead, the structural units are built up by grains having low-Σ grain boundaries to each other and additional smaller grains in the centre and/or orientation gradients in some of the involved grains accommodate for internal stresses. Changing only one of orientation relationships between neighbouring grains would cause other (energetically favourable) low-Σ boundaries to disappear and be replaced by (energetically less favourable) random grain boundaries. Overall, the formation of these distinct structural units seems to be energetically favourable (low-Σ boundaries) as they are still present and dominate the microstructure after annealing (see Fig. 4). In fact, similar structural units were observed after annealing the material for 20 min at 600°C [16]. However, the performed annealing treatments were obviously not sufficient to create 5-fold twins, which are expected to be energetically the most favourable configuration. Overall, the microstructure development is different from what was observed in Nickel electrodeposits having another initial texture. In those materials, twinning is observed to form new, fast growing, low energy grain orientations dominating the final texture. In the <110> textured material, in contrast, the twins stabilize the grain configuration.

An attempt was made to investigate the structural units in three dimensions. This was done by localizing the structural unit of interest by use of EBSD, marking the position with help of an indent, and then electropolishing the material step-wise. For determining how much material was removed, a silver paint droplet was put on the surface before electropolishing. After the polishing step, the remaining droplet was removed and the height difference between the location of the droplet (initial surface) and the electropolished surface at the location of the structural unit was measured with help of a Wyko Optical Profiler. It was possible to perform three consecutive polishing steps of 1 µm, 1 µm and 1.5 µm, respectively. Hence, it is possible to perform 3-dimensional measurements in this way. However, the orientation maps were partly distorted due to drift and the grains of the structural unit were more or less the same over the measured depth of 4.5 µm, i.e. the area of interest in the

centre of the structural unit was not captured. This means, that 3D EBSD measurements by employing focused ion beam and/or investigations by TEM are required for achieving better resolution and for being able to fully and reliable describe the (3-dimensional) grain arrangement in the structural units.

4. Summary and conclusion

Pulse-electrodeposited Nickel with sub-microcrystalline microstructure and a <110> fibre texture in growth direction was investigated. By use of EBSD, structural units consisting of grains possessing a common <110>-zone axis in growth direction and low-Σ grain boundaries (often twins) between each other have been found in the microstructure. The grain boundaries of the structural units have been found to be strongly connected, i.e. changing only one of the orientation relationships between neighbouring grains would cause other low-Σ boundaries to disappear and be replaced by energetically less favourable random grain boundaries. Even though grain growth sets in above 325°C, the structural units remain in the microstructure and the <110> fibre texture is conserved up to at least 600°C. This means that the grain boundary arrangement can be held responsible for the preservation of both the structural units and the <110> texture (low energy configuration even though some stress is involved). In this case there is no orientation change (e.g. by twinning) when grain growth occurs as seen in previous studies on Ni and Ni-Fe of different initial texture. The occurrence of structural units in form of 5-fold twins (parallel to growth direction) seems to be a special case and has not been observed, yet.

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