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Columns formed by multiple twinning in nickel layers—An approach of grain boundary engineering by electrodeposition

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Complementary microscopic and diffraction based methods revealed a peculiar microstructure of electrodeposited nickel. For the as-deposited layer, thus, without any additional treatment, multiple twinning yields a high population of Σ3n boundaries, which interrupts the network of normal high angle grain boundaries. A peculiar arrangement of Σ3 boundaries forming five-fold junctions is observed. The resulting microstructure meets the requirements for grain boundary engineering. Twinning induced effects on the crystallographic orientation of grains result in one major texture component being a ⟨210⟩ fiber axis and additional minor orientations originating from first and second generation twins of ⟨210⟩, i.e., ⟨542⟩ and ⟨201⟩.

The present work reports about grain boundaries and multiple twinning of a 16.5 μm-thick nickel layer with ⟨210⟩ fiber texture, electrodeposited onto an amorphous Ni-P substrate. Electrodeposition was carried out from a Watts electrolyte consisting of 300 g/dm³ NiSO₄ · 7H₂O, 35 g/dm³ NiCl₂ · 6H₂O, and 40 g/dm³ H₃BO₃. The pH of the electrolyte was 2.5, vigorous mechanical stirring was applied and the deposition temperature was kept constant at 323 K during electrodeposition. The applied current density was 10 A/dm².

For quantitative crystallographic texture analysis, X-ray diffraction (XRD) pole figures of 111, 200, and 220 reflections were measured with Cu-Kα-radiation (Diffractometer D8 Discover, Bruker AXS). The azimuth angle φ was varied from 0° to 360° in steps of 5°; the sample tilt given by the pole angle θ was varied from 0° to 75° in steps of 5°. Measured intensities were corrected for background and a Ni-powder standard was used for defocussing correction. Following,⁰ the complete 3D orientation distribution function was calculated, but as the sample has a fiber texture in the direction of layer growth (normal direction, ND), the inverse pole figure in ND fully characterizes the texture in the deposit. As shown in Fig. 1(a), the major texture component is ⟨210⟩ with an orientation density of 3.8 m.r.d. (multiples of random distribution). This fiber texture is rather broad with a deviation of 9.4° around the ideal fiber axis. In addition to the major ⟨210⟩, two minor components close to ⟨542⟩ and ⟨711⟩ with orientation densities of 1.4 and 1.2 m.r.d., respectively, are identified. Calculating the twin orientation relations in FCC shows that these three orientations are related to one another by a twinning operation. The first generation of twins originating from ⟨210⟩ is either ⟨210⟩ or ⟨542⟩; and the first generation of twins from ⟨542⟩...
are \(\langle 210 \rangle, \langle 16 10 7 \rangle, \langle 25 15 6 \rangle, \) and \(\langle 20 2 1 \rangle\). Since the angular difference between \(\langle 16 10 7 \rangle\) and \(\langle 542 \rangle\) is \(7.0^\circ\) and that of \(\langle 25 15 6 \rangle\) and \(\langle 542 \rangle\) is \(9.4^\circ\), and the maxima in the inverse pole figure are broad (e.g., large spread around \(\langle 542 \rangle\), Fig. 1(a)), \(\langle 16 10 7 \rangle\) and \(\langle 25 15 6 \rangle\) cannot be resolved separately and are approximated by \(\langle 542 \rangle\). Similarly, there is only a slight deviation from the calculated \(\langle 20 2 1 \rangle\) orientation and the experimentally measured orientation maximum. In Fig. 1(b), \(\langle 210 \rangle, \langle 542 \rangle,\) and \(\langle 20 2 1 \rangle\) are shown by yellow, light blue, and light red dots, respectively. Taking into account the broadness of the \(\langle 210 \rangle\) fiber component, twinning operations of \(\langle 210 \rangle \rightarrow \langle 542 \rangle\) and \(\langle 542 \rangle \rightarrow \langle 20 2 1 \rangle\) are also calculated for other orientations close to the ideal fiber axis (black and gray lines around the \(\langle 210 \rangle\) in Fig. 1(b)). It is noted that further possible twinning such as \(\langle 210 \rangle \rightarrow \langle 210 \rangle, \langle 542 \rangle \rightarrow \langle 210 \rangle,\) etc. are not considered in the calculations. Nevertheless, despite the apparent deviation, there is a satisfactory agreement between the expected twin components and the measured textures. Hence, the global XRD analysis, i.e., averaging over about the whole layer thickness, strongly suggests that up to the second generation of twins originating from the major texture component are present in the microstructure.

To investigate the local texture and examine the character of the grain boundaries, electron backscatter diffraction (EBSD) and ion channeling imaging (ICI) were performed in a FEI Helios NanoLab™ 600, equipped with an EDAX-TSL EBSD system and a Hikari camera. The EBSD measurement was performed in a hexagonal grid with an electron probe current of 5.5 nA at an acceleration voltage of 12 kV, with step size of 25 nm. The cleaning procedure of the measured data was applied using OIM 5™ as follows: (i) grain confidence index standardization, (ii) single iteration grain dilation (in both cases, a grain was defined as a region consisting of at least four connected points with misorientations of less than \(5^\circ\)), (iii) all the data points with confidence index below 0.1 were disregarded. The ICI investigation was performed using \(\text{Ga}^+\) ions with an energy of 30 keV and ion density of \(2.6 \text{C/m}^2\) on the same location, where the orientation map was acquired beforehand for supplementary characterization at higher resolution. Images covering the whole thickness of the deposit are shown in Fig. 2. Based on the ion channeling image (Fig. 2(a)), the grain size is estimated to be below 50 nm in the near-interface region (the first \(1 \mu\text{m}\) of the layer). Consequently, in this region no reliable information was obtained with EBSD for the current conditions, as is reflected by the ragged appearance and the relatively many non-indexed pixels (white regions in the orientation map, Fig. 2(b)). At a thickness of \(1 \mu\text{m}\), relatively large grains with characteristic straight boundaries have developed. With increasing distance from the substrate, the grain size increases, but the same characteristic straight boundaries remain. The orientation map in Fig. 2(b) shows that most of those straight boundaries are \(\Sigma 3\) boundaries (shown in black). Furthermore, it shows that the microstructure is composed of \(\langle 210 \rangle\)-oriented columns (yellow to yellowish green) and that the \(\langle 210 \rangle\)-oriented columns consist of a chain of \(\langle 210 \rangle\)-oriented grains, which are separated by \(\Sigma 3\) boundaries and, thus, must be a result of repeated and multiple twinning.

In Fig. 3, one column of \(\langle 210 \rangle\)-oriented grains and its neighboring grains is highlighted and shown as an orientation map (Fig. 3(a)). It is evident from Fig. 3(a) that a \(\langle 210 \rangle\)-oriented grain is twinned into another \(\langle 210 \rangle\)-oriented grain, which at its turn twins into another \(\langle 210 \rangle\) grain. Accordingly, a column dominated by \(\langle 210 \rangle\)-oriented grains is the result of \(\langle 210 \rangle \rightarrow \langle 210 \rangle\) twinning. Clearly \(\langle 542 \rangle\)-oriented grains (in light blue/purple color) are bounding the \(\langle 210 \rangle\)-oriented...
is beneficial for enhanced grain boundary specific properties, whereas the latter is deteriorating mechanical strength. Hence, thickness should be optimized as a trade of between the two for different applications. In addition to thickness, careful selection of electrodeposition conditions can significantly influence multiple twinning and, hence, the resulting microstructure. The origin of multiple twinning is not completely understood yet. For the applied deposition conditions, i.e., low pH and high current density, hydrogen evolution is favored. Thus, it is suggested that the evolution of H$_2$, at the cathode/electrolyte interface plays a role.

A peculiar observation is that in the regions with abundant $\Sigma$3 boundaries a five-fold junction of straight boundaries occurs. In Fig. 3(b), a network of grain boundaries in such a region is shown and two of the five-fold junctions are marked by the black rectangles. EBSD analysis identified the occurrence of $\Sigma$9 boundaries, with length of 2–3 pixels (50–75 nm) in the center of a five-fold junction of $\Sigma$3 boundaries. Altogether five $\Sigma$3 boundaries meeting in a single point would span a total angle of 352.6°, only 7.4° from a full rotation. Then, it might be suggested that the closing angle of 7.4° is compensated by the occurrence of a small $\Sigma$9 boundary, so that no actual five-fold junction occurs.

However, TEM investigations in a Titan 80–300 field emission TEM, from FEI operated at 300 KV, in HAADF-STEM mode, show that the five boundaries actually do meet in the center of five-fold junctions, see Fig. 3(c). Hence, the $\Sigma$9 boundaries identified in the orientation map at the center of a five-fold junction are merely an artifact, caused by the choice of a hexagonal grid for measurement of the orientation map (up to 3 boundaries can meet in one point in such a grid). Thorough analysis of $\Sigma$9 boundaries as well as the thermal stability of the layers consisting of numerous and multiple twins are of high importance and will be addressed elsewhere.

Summarizing, it was demonstrated by combining XRD texture measurements and local orientation analysis by EBSD that electrodeposition of nickel from a highly acidic Watts electrolyte and high current density, results in multiple twinning of $\{210\}$ oriented grains. This yields the development of peculiar $\{210\}$ columns with sequences of twins within individual columns and, thus, a high number of $\Sigma$3 boundaries separating the grains forming these columns. Finally, by careful selection of electrodeposition conditions, grain boundary engineered material can be achieved.

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