Investigation of anomalous grains in polynanocrystalline nickel

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Abstract. Polynanocrystalline nickel, with an as received grain size distribution in the range 30 to 80 nm, when heat treated at a temperature of 500°C causes overall coarsening of the grains and anomalous growth of some grains. This leads to a bimodal grain size distribution. The anomalous large grains, typically 75-100 µm, have an angular morphology that is not typical of the polyhedral grains within the overall distribution. Using a combination of focus ion beam milling and imaging, and electron backscatter diffraction it has been established that the interfacial planes forming the overall grain boundaries for these anomalous large grains include 110, 210, 112 and 310 planes. In addition a substructure is produced within the large grains interrelated in size with the subsumed nano-scale grains. The results are discussed briefly with respect to the more energetically favourable 111 boundary planes and the overall mobility.

1. Introduction
Polynanocrystalline materials are those with a structure of grains with a sub 100 nm size. In general such materials have improved mechanical properties compared with the corresponding microscale materials. These materials have high yield strength and hardness but are less ductile than their poly-macrocrystalline cohorts [1]. Whilst the materials are important for potentially a range of applications, the presence of high energy grain boundaries promotes coarsening to reduce the overall energy of the system [1]. Previous work has shown that a bimodal grain distribution with a polynanocrystalline structure embedded with larger grains retained the hardness associated with the smaller grains and improved the ductility [2]. Previous investigation showed that heat treatment of polynanocrystalline nickel causes a bimodal grain structure to develop; a coarsened matrix of smaller grains and large anomalous grains [3]. This paper considers polynanocrystalline nickel grain coarsening following heat treatment at temperatures of 420°C and 500°C for various times and the resulting bimodal grain structure. Primary interest comes from the angular anomalous grains with planar grain boundaries.

2. Experimental Procedure
The polynanocrystalline nickel was obtained from Integran Ltd and is proposed to be produced by pulsed electrodeposition to a thickness of 2 mm. This method of creation can introduce impurities into the material, predominantly sulphur. Energy dispersive x-ray spectroscopy (EDX) of a large area of the sample shows that there are traces of sulphur present in the...
material. As received material has no texture and when studied by x-rays diffraction (XRD) gives a grain size of 30-80 nm. Coarsening of the nano-scale nickel has been considered following heat treatment at temperature of 420°C and 500°C in vacuum, table 1. The microstructure changes have been characterised using a combination of transmission electron microscopy (TEM) using a Philips EM430 transmission electron microscope working at 200kV and focus ion beam (FIB) milling and imaging using a FEI Helios dual beam workstation and electron backscattered electron diffraction (EBSD) in a Zeiss Evo scanning electron microscope(SEM).

3. Results

3.1. Grain Growth

The grain structure of the as received polynanocrystalline nickel can be seen in Figure 1. The TEM image of the material, with the corresponding electron diffraction pattern, displays the grain size of 30 to 80 nm and containing the FCC crystal structure. This image is diffuse due to overlapping contrast caused by the number of grains that are contained in the 150nm thick foil section. An initial matrix of heat treatments lead to coarsening of the nano-grains and in one case a bimodal distribution including both the coarsened grains and large anomalous grains, figure 2. This was by achieved heat treating a sample at 500°C for 3 hours; table 1 shows the heat treatments and the average grain size measured by linear intercept. As such the average grain size for 3 hours at 500°C has been split for the bi-modal nature of the specimen, denoted in table 1. Specimens which have a bimodal grain size distribution developed the larger anomalous grain size of the order of 30-50 µm where the size of the coarsened matrix grains surrounding them are 500-600nm. In order to find a temperature dependence at a heat treatment time of 3 hours further work was then done using a known constant temperature gradient held over the sample. This isothermal heat treatment allows investigation of the relative temperatures that cause both grain coarsening and the anomalous grain growth. EBSD mapping, shown in figure 2, reveals the microstructure of coarsened grains and anomalous grains. As table 1 shows, the size of the coarsened matrix does not increase at longer time however anomalous grains appear. From investigation of the sample which was held with a temperature gradient across it for 3 hours it was deduced that the anomalous grain growth occurs from 485°C, and matrix grain coarsening from 400°C [4].

Table 1: Average grain size measured by linear intercept method, including the bi-modal system developed at 500°C for 3 hours.

| Sample     | Average Grain Size (nm) | Standard Deviation |
|------------|-------------------------|--------------------|
| virgin     | 95                      | 65                 |
| 420°C 10 mins | 580             | 150                |
| 420°C 3 hrs   | 510              | 70                 |
| 420°C 12 hrs  | 540             | 90                 |
| 500°C 10 mins | 630             | 160                |
| 500°C 20 mins | 680             | 400                |
| 500°C 3 hrs   | 520             | 340 coarsened matrix |
| 500°C 3 hrs   | $4.0 \times 10^3$ | $2.9 \times 10^3$ anomalous grains |

3.2. Anomalous Grains

To gain knowledge about the planar faces of anomalous grains requires two surface analysis. A combination of SEM and EBSD is used to identify, and find the orientation of, large anomalous grains. With this knowledge of the grain surface and with FIB milling to reveal the relative
angle of the second face extending into the material, figure 3, allows for two surface analysis and calculation of the orientation of the grown plane. Hence, given an angle between planes, the orientation of one and the fact that the two planes have a common edge direction there is unique solution for the grain boundary relative to the anomalous grain. Further ESBD investigation addressing miss-orientation within the large anomalous grains has discovered small (°5 degrees) variations in orientation, figure 4. This shows between 0 (blue) and 5 (red) degrees, green 1 degree, small regions of miss-orientaion in the anomalous grain and thus a substructure with cells typically ~500nm which are of a similar size to the surrounding matrix grains. The colours shown in the EBSD image, figure 2, represent the orientation of the grains determined by the position of the kikuchi bands relative to the pattern that would be produced by a 100 plane. The FIB milled section, figure 3, shows a large grain and the angle this plane has with respect to the top surface and milled surface. Given this geometric information and the orientation of the grain from the EBSD these planar boundaries were evaluated, table 2. This shows that the majority of planes are 211 together with other planes and gives a 94% confidence that there are no low index 111 planes present.

Table 2: All measured growth planes associated with anomalous grains

| Number | Plane          |
|--------|----------------|
| 8      | 211            |
| 4      | 210            |
| 3      | 221            |
| 2      | 110, 310, 320  |
| 1      | 311, 322, 430, 432 |

4. Discussion
The abnormally large grains observed as part of the coarsening of the nano-scale nickel have an unusual morphology with planar faces. These grain faces give a range of planes, table 2, that do not include the low energy, close packed 111 plane. These planar faces of the anomalous grains are formed and advance through the grain coarsened matrix. As such the driving force will be a balance between more energetically stable and crucially more mobile grain boundaries. The mobility of a grain boundary may be considered with respect to the ease of adding atoms to the boundary plane. For example, a 211 plane will contain stepped ledges that facilitate growth. Clearly the presence of a substructure within the larger grains of a dimension equal to that of the smaller surrounding grains implies some local interactions occur. However, since the grain boundaries are overall planar suggests that they act as if growing with an average interfacial energy; akin to a grains growing from a liquid. It is proposed to be due to impurities at the boundary, mainly sulphur, changing the boundary energy, making it more anodic and thus weaken the nickel-nickel bonds [5]. High resolution STEM-EDS of microanalysis of thin sections has confirmed the increased concentration of sulphur present at the anomalous grain boundary [6]. This will encourage growth of the more energetically favourable larger grain. In extreme cases where the sulphur concentration is sufficiently high a wetting transition has been proposed to accelerate grain boundary movement [7, 8]. In some cases where there is a very low angle boundary, for example a Σ3 boundary, the advancing grain boundary sweeps round and engulfs the smaller grain, figure 2.

5. Acknowledgments
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Figure 1: Bright field TEM image of the as received polynanocrystalline nickel, insert—diffraction pattern.

Figure 2: EBSD image of the nickel sample displaying a bi-modal grain size distribution after a heat treatment of 500°C for 3 hours.

Figure 3: Image of the FIB cut used to reveal the angle between planes.

Figure 4: EBSD image showing up to 5 degrees misorientation within an anomalous grain.

6. References

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