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Growth of abnormal planar faceted grains in nanocrystalline nickel containing impurity sulphur

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Abstract

The grain size of nanocrystalline nickel containing 280 ppm S produced by electrodeposition has been established by electron microscopy to be ~50 nm. The growth of these grains has been studied using a range of isothermal and isochronal heat treatments. Initially grain coarsening was observed to occur at temperatures in the range of 300–500 °C, with an activation energy of 72.9 ± 13.4 kJ mol^{-1}. At temperatures above 485 °C the coarsening was followed by the formation and growth of abnormally large grains, ~40 μm, which are geometrically distinct. The microscale facets are crystallographically specific planes related to the abnormal grain, not the local coarse grain matrix. Details of the coarsening, formation and growth of the grains has been quantified using a range of techniques, including transmission electron microscopy, electron backscatter diffraction, energy-dispersive X-ray spectroscopy and focused ion beam milling and imaging. The overall changes in the microstructure are considered to occur in three steps: (1) grain coarsening; (2) abnormal grain formation; and (3) abnormal grain growth. The underlying mechanisms controlling steps (2) and (3) are discussed with respect to the role of impurity sulphur on the nickel atom bond strength within the grain boundary volume.

Keywords: Nanocrystalline nickel; Grain coarsening; Abnormally large grains; Sulphur impurity; Electron optical techniques

1. Introduction

Nanocrystalline (nc) materials display specific mechanical, physical and chemical properties that are significantly different from those of equivalent microscale polycrystalline materials [1–3]. It is established that the major cause of the special properties in these nc materials, such as improved strength, heat capacity and magnetic properties, can be attributed to the large volume fraction of atoms that occupy grain boundaries compared with the microscale materials [4–6]. The nanoscale state is far removed from equilibrium and it is this condition that explains the intrinsic instability of these nc materials, for example when subject to thermal exposure. It is noteworthy that a material with a mean grain size of 30 nm will consist of ~18% grain boundary volume, compared with ~1% for grain sizes of ~500 nm [7]. Hence, it is important to characterize the evolution of grain size during annealing of nc materials, since the stability, mechanisms and kinetics of coarsening may differ from those associated with the microscale.

Grain growth in polycrystalline materials has been studied extensively and is driven by a reduction in total energy of the system through the removal of grain boundaries and dislocations [5,8,9]. This study focuses on Ni, which has a face-centred cubic (fcc) crystal structure and melts at a temperature of 1453 °C [10]. The activation energy of self-diffusion for polycrystalline nickel is 109 kJ mol^{-1}; however, this can be altered by the presence of impurity elements, such as sulphur [11]. This change in self-diffusion activation energy was studied by Błaszczyszyn for a system

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with a known concentration of impurity sulphur atoms [12]. Polycrystalline Ni with varying percentages of a monolayer coverage of S when heat treated over a temperature range from 200 to 320 °C showed different growth activation energies: 113.4 ± 15.1 kJ mol^{-1} for a 30% coverage of sulphur, 165.3 ± 6.7 kJ mol^{-1} for a 70% coverage and 352.7 ± 14.2 kJ mol^{-1} for full surface coverage. This increase is attributed to participation of sulphur–nickel complexes in the self-diffusion mechanism [12]. Grain growth in microscale polycrystalline materials is dominated by migration of curved grain boundaries towards the centre of curvature whilst maintaining the balance of tension at the grain edges and corners. It is well established that deformation prior to heat treatment can lead to anomalously large grains forming at a critical value of pre-strain [13,14]. However, if this critical value is exceeded, a relatively uniform distribution of small grains is formed.

Grain growth in nc materials can be due to rotation and coalescence of adjacent grains, as well as normal grain boundary movement [5,9]. It is well established that the speed of grain boundary movement at a specific temperature is affected by the presence of impurity atoms [5,9]. Boundaries can be pinned by some types of impurity atoms to reduce mobility and stabilize the grain size, whereas other elements increase the mobility, leading to grain growth [5,9]. Grain boundary pinning has been used to inhibit growth and control the grain size of nc materials produced via electrodeposition. Matsui et al. showed that increasing the carbon content and or the sulphur content in the bulk material produced a smaller grain size [15]. In microscale polycrystalline nickel, impurity sulphur can segregate to grain boundaries when subjected to either equilibrium or non-equilibrium thermal conditions [16,17].

There have been many studies concerning the segregation of sulphur to grain boundaries in nickel and the resultant effect on embrittlement [18,19]. Mahalingam et al. confirmed this for microscale polycrystalline nickel [20]. Larere et al. established the kinetics and the activation energy for sulphur segregation to both grain boundaries and free surfaces in nickel, and determined values of 98 and 180 kJ mol^{-1}, respectively [21]. Allart et al. considered grain boundary segregation of sulphur in nickel using a combination of Auger electron spectroscopy and wavelength-dispersive X-ray spectroscopy to establish a segregation enthalpy, δH, of -93.9 ± 2.5 kJ mol^{-1}, and the grain boundary concentration at saturation (0.97 ± 0.09) of a monolayer, where the monolayer is 65.8 ± 6.1 ng cm^{-2}, over a temperature range from 550 to 900 °C [22]. Floreen and Westbrook conducted work on microscale polycrystalline nickel with sulphur levels from $\leqslant 1$ to 50 ppm [23]. No distinct phases were associated with the equilibrium segregation of sulphur to the grain boundaries. However, grain boundary hardening was observed, and an unusual variation to the Hall–Petch relationship was established when conducting tensile tests within a grain size range of 0.3–1 mm [23].

The effect of sulphur segregation to a grain boundary was modelled by Briant and Messmer for a typical high-angle grain boundary where sulphur atoms are located at interstitial atom sites [16]. In this case the S atoms were located within a tetragonal dodecahedron (a ten triangular sided polyhedron) of nickel atoms. Molecular orbital theory was used to solve the electronic structure of a cluster of Ni atoms with and without S atoms. The model shows a change in the possible energy levels of the system and plots of the molecular orbital contours reveal strong bonding to the sulphur atoms by nickel atoms which relatively weakens the bonds between the neighbouring nickel–nickel atoms [16]. Crampin et al. showed a similar reduction in nickel bonding in a model of S substitutionally in a $\Sigma 5$ grain boundary [24]. Yamaguchi et al. revealed that, in models of boundaries containing 0–100 ppm S, a greater sulphur concentration leads to a smaller tensile yield stress, consistent with the reduction in binding energy with higher concentrations of sulphur [25]. Phosphorus segregated to iron grain boundaries was shown by Brown et al. to significantly reduce the cohesive energy. This promotes intergranular fracture because of electron transfer between the iron and phosphorus atoms, resulting in the iron atom bond becoming weaker in the segregated grain boundary volume. The grain boundary becomes more anodic with the increasing presence of phosphorus [26]. A similar electron change transfer mechanism would be associated with the nickel–sulphur system [27].

In this paper we consider grain growth in an electrodeposited nc nickel containing a significant concentration of impurity sulphur. The experimental procedures and results are described in Sections 2 and 3. The role of sulphur in promoting unusual grain growth in this nc nickel is discussed in Section 4.

2. Experimental

2.1. Material

Nanocrystalline nickel, in the form of a 50 mm × 50 mm × 0.5 mm sheet produced by electrodeposition, was obtained from Integran Technologies Ltd (Mississauga, Canada). This contained 280 ppm sulphur, as measured by combustion and infrared analysis. The grain size distribution is within the range from 30 to 80 nm, with no evidence of crystallographic texture [28]. The initial microstructure was subsequently altered by heat treatment either isothermally for different times in an air furnace or isochronally for a fixed time at different temperatures by electrical resistance heating in a nitrogen atmosphere. The isochronal heat treatments were conducted at the National Physical Laboratory (NPL; Teddington, UK) using a specially designed rig. The rig is an electrothermomechanical test developed at NPL which allows resistivity to be measured over a range of temperatures with variable applied load. In this case it was used at zero load with test specimens, typically 40 mm × 5 mm and 0.5 mm, held with

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