The ductile–brittle transition for nominally pure polycrystalline nickel

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ABSTRACT

A ductile to brittle transition has been observed for a nominally high purity polycrystalline nickel of $\sim 200\,\mu m$ grain size, containing 50 ppm sulphur. The nickel specimens were subjected to heat treatment at 1017 °C for 0.5 h and were then either furnace cooled or water quenched. Small notched bend geometry specimens were tested over the temperature range of −196 °C to 200 °C at a fixed strain rate. Both the work to initiate fracture and the proportion of intergranular fracture were determined. The elemental concentration of sulphur at the grain boundaries has been measured using scanning Auger spectroscopy and STEM-EDX microanalysis. These compositions are compared with predictions from a non-equilibrium segregation model. The segregation of sulphur to the grain boundaries has a strong effect in promoting brittle intergranular fracture and this is attributed to the change in cohesive strength of the grain boundaries as a result of the segregation.

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1. Introduction

Crack initiation and propagation in polycrystalline metals and alloys can be characterised by the balance between a driving force and a resistance [1]. The former is proportional to the energy available for fracture and equals the mechanical work done minus the kinetic and potential energy per unit area of crack extension. The resistance is a material characteristic that has to be exceeded to allow the crack to extend. As a minimum, this is equal to the energies of the surfaces created (possibly, allowing for re-structuring of bonds when the surfaces are created). Grain boundaries are one of several microstructural features that resist transgranular brittle crack propagation. However, they can provide a low resistance path for intergranular fracture if the boundary cohesive energy is reduced to below a critical value, for example, due to the presence of certain minor alloying or impurity atoms [2]. Typically crack initiation and propagation mechanisms vary with temperature in polycrystalline materials leading to failure by brittle fracture at lower temperatures and ductile fracture at relatively higher temperatures [1,3]. This is referred to as the brittle to ductile transition. In general, it is considered that because of the greater number of slip systems available in fcc metals and alloys they are less likely to undergo brittle fracture [4,5,6]. Indeed Kelly et al. [7] considered that if an atomically sharp Mode1 crack in a solid containing no other imperfections can easily emit dislocations from the tip before a crack can extend by cleavage then the solid is intrinsically ductile. FCC metals including nickel fall within this category.

Since nickel has a fcc crystal structure it would be expected to be intrinsically ductile, but observations of brittle intergranular fracture at room temperature have been associated with either grain boundary embrittlement [8] or high strain rate loading [9]. The former arose from specific heat treatments that resulted in segregation of impurity sulphur to free surfaces and grain boundaries. According to Seah and Hondros [10] sulphur has low solubility in nickel and a high grain boundary enrichment ratio of $\sim 10^4$. The study of sulphur segregation kinetics by Larere et al. [11] showed that the grain boundary segregation energy for this element is equal to about half that for a free surface. Lassila and Birnbaum [12] studied the synergistic effect of segregation of hydrogen and sulphur in nickel where the bulk hydrogen concentration required for intergranular fracture is decreased by the presence of sulphur at the grain boundaries. In their study it was proposed that multi-layer sulphur segregation extending over a width about a boundary of $\sim 5\,nm$ leads to intergranular fracture. By comparison mono-layer coverage where the width is $\leq 0.5\,nm$ does not cause intergranular fracture in the absence of hydrogen. It is noteworthy that Zhang et al. [13] observed that phosphorus also contributed to the promotion of intergranular fracture within nickel. It was proposed that the phosphorus influenced the kinetics of surface segregation of sulphur in nickel because of site competition between these two elements.

In general, segregation of impurity and minor alloying elements can modify the susceptibility of polycrystalline metals and

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alloys to intergranular fracture by changing the local cohesive strength. It has been shown for many materials that both equilibrium and non-equilibrium segregation of specific elements to grain boundaries can either strengthen, (e.g. boron segregation in copper), or weaken, (e.g. phosphorus segregation in steel), the boundaries and thereby reduce or increase susceptibility to brittle intergranular fracture [14,15]. The underlying chemical and physical mechanisms for sulphur-induced intergranular embrittlement of nickel have been considered by Messmer and Briant [16]. Quantum mechanical calculations indicate that sulphur draws electrons from the Ni–Ni metal bond and, thereby, reduces the cohesive strength of the grain boundaries. Recently, a large-scale molecular dynamic simulation using many-body interatomic potentials for Ni–Ni, S–S and S–Ni interactions showed that segregation of sulphur induced amorphization at grain boundaries with an associated reduction in the calculated work of interfacial separation, cohesive energy, from 1.65 J/m^2 for pure Ni to 1.20 J/m^2 [17]. Heuer et al. [18] performed notched geometry tensile tests at room temperature on polycrystalline Ni with different bulk concentrations of sulphur following a heat treatment at temperatures in the range of 625–1000 °C. The fracture was ductile at low concentrations of sulphur, but if the concentration at the grain boundary exceeded $\sim$15.5 $\pm$ 3.4 at% brittle intergranular fracture was induced at room temperature. First principle calculations based on uniaxial tensile loading carried out by Yamaguchi et al. [19] also identified that a critical concentration of sulphur between 9 and 14 at% was needed for decohesion of grain boundaries. This concentration corresponds to about 1.5–2 monolayer coverage and is in reasonable agreement with experimental observations [18]. In addition, the simulations showed that the repulsive forces between sulphur–sulphur atoms led to local expansion and decohesion at the grain boundaries.

In this paper we explore the ductile to brittle fracture transition temperature (DBTT) for nominally pure nickel containing a low concentration of impurity elements, in particular sulphur. In Section 2 we describe the material and experimental procedures used. The results are presented in Section 3 for nickel subjected to a furnace cool or a water quench from a temperature of 1017 °C followed by fracture in a bending mode over the temperature range −196 °C to 200 °C. The results are discussed in Section 4 with respect to the observed ductile to brittle transition temperature for the two heat treatment conditions and the underlying mechanisms associated with impurity element segregation to grain boundaries in nickel. Conclusions are presented in Section 5.

2. Experimental procedure

2.1. Material

A nominally pure polycrystalline nickel rod, 12 mm diameter, obtained from Goodfellow Metals Ltd (Cambridge, UK) has been used for the present investigation. The chemical analysis in atomic percentage for this material is given in Table 1. Two sections of rod were given a grain size stabilisation heat treatment in air at the temperature of 1017 °C for 0.5 h and then one was water quenched (NQ) and the other furnace cooled (NA) to

Table 1
Elemental chemical composition of nominally pure polycrystalline nickel (at%).

Element	Cu	Fe	Mn	Si	S	P	O	Ni
at%	0.009	0.01	0.12	0.04	0.005	0.0008	0.16	Bal

room temperature over a period of 2 h. The mean linear intercept grain sizes for as-received and heat treated material were 40 $\pm$ 10 μm and 207 $\pm$ 33 μm respectively.

2.2. Three point bend test

A range of small-scale specimen mechanical tests have been reviewed by Lucas [20]. They include bend geometry specimens for the evaluation of strength and fracture. Based on the Lucas conclusions three-point bend geometry specimens were extracted from the heat treated sections of the 20 mm diameter nickel rod by electric discharge machining (EDM). The specimens were removed with an orientation with respect to the original nickel rod as shown in Fig. 1(a). The specimens were 16 mm long and 4 mm × 4 mm cross-section, Fig. 1(b). A sharp notch in the traverse orientation, Fig. 1(a), was cut to a depth of a third the width of the specimen (a/w=1/3) by EDM with a wire of 0.1 mm diameter. This procedure ensured that the notch depth was reproducible to with $\pm$ 2%. The tests were conducted using a Zwick tensometer (load cell range 0–10 kN), equipped with an environmental chamber able to operate over the temperature range of −196 °C to 400 °C. The temperature was controlled and monitored by a chromel/alumel thermocouple positioned within the environmental chamber. An additional thermocouple was attached to the bend jig to ensure that the temperature of the specimen was maintained to within $\pm$ 3% of the set temperature. The specimens were deformed under displacement control at a rate of 8.33 μm s^{-1} measured from the cross-head. Replicate tests (maximum three specimens) were conducted at each selected temperature.

2.3. Material characterisation

The fracture surfaces of the test specimens were examined using a Hitachi S-2300 scanning electron microscope operating at a voltage of 25 keV. A magnification of × 500 was selected to measure the total projected area of the intergranular fracture facets using a procedure that involved drawing equi-distant lines on these images and measuring the per cent of intergranular facets that intercepted these individual lines [21]. Energy dispersive X-ray microanalysis was undertaken using a Link spectrometer interfaced to the SEM. A high resolution FEI Helios Dual Beam work station was also used to undertake focused ion beam milling and imaging. The images were recorded at an operating voltage of 30 keV and a current of 70 pA. The milling was
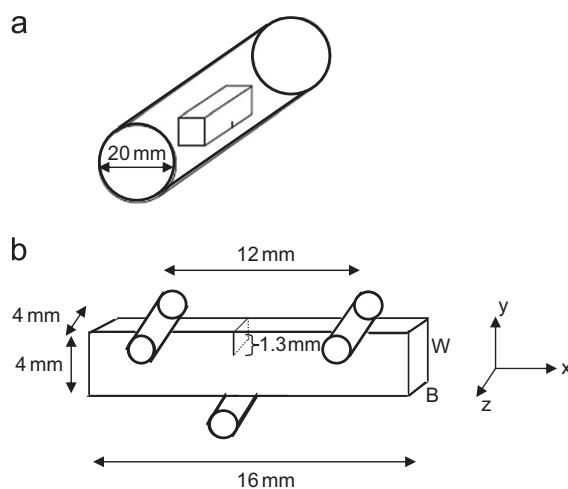

Fig. 1. Schematic diagram of the 3-point bend specimen (a) orientation in with respect to the original nickel bar and (b) giving the dimensions.