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Grain boundary segregation in binary nickel–bismuth alloy

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ABSTRACT

Grain boundary segregation and segregation kinetics are investigated by means of atom probe tomography in a binary Nanocrystalline nickel-bismuth alloy. Gibbsian excess and width of segregation layers at grain boundary are quantitatively determined. If segregation is approximated by McLean kinetics, remarkably fast volume transport of bismuth is derived. However, details of the segregation kinetics are in significant contrast to the McLean model. Additional influence of attractive Bismuth interaction is indicated. The experimentally demonstrated clear segregation tendency suggests that reported embrittlement of Ni–Bi alloys is due to significant grain boundary segregation of Bi. Diffusivity of Bi in nanocrystalline Ni and segregation amplitude were found to be $D_B \approx (2.16 \pm 0.48) \times 10^{-21}$ m^{2}s^{-1}, and 17 respectively.

1. Introduction

Nickel (Ni) based alloys are advanced structural materials that are mainly used in aircraft engines but are also applied in the chemical, petrochemical and electrical industries [1,2]. Because of their undesired embrittlement at intermediate temperatures, these alloys were already subject of extended studies [3–6]. Many researchers [7,8] considered the intermediate temperature embrittlement (ITE) of Ni-based superalloys to be caused by the evolution of intergranular precipitates. However, several experiments demonstrated that commercially pure or only weakly alloyed Ni also show evident ITE [9,10]. In this case, the interpretation of intergranular precipitates is doubtful. Alternatively, it has been suggested that this embrittlement is related to equilibrium grain boundary (GB) segregation [11], or possibly even kinetically driven non-equilibrium segregation [12,13].

GB segregation is the enrichment of GBs by impurity atoms during an annealing treatment. Because of a strong segregation tendency, even very small amounts of antimony, phosphorus, tin, or sulphur can cause an undesired embrittlement in iron and nickel based alloys [14]. On the other hand, small amounts of boron, molybdenum at GBs can increase the ductility of steels [15]. Interfacial chemistry also affects mobility, GB energy, and the stability of nanostructures [16,17]. Local solute decoration may lead to the nucleation of second phases, creation of complexions [18], or choosy melting of GBs [19]. Moreover, semiconductors are distressed by GB segregation owing to band structure fluctuations that alter the recombination motion of charge carriers [20]. The study of Copper (Cu) embrittlement by GB segregation of Bismuth (Bi) has a long history [21,22]. However, the Ni(Bi) is also an interesting system, due to its phase diagram similarity with binary Cu(Bi) alloy and because of its vast industrial application [23,24]. In a previous article [13] we had proven, that, while high purity Ni shows no ITE, even an amount as small as 25 wt ppm of Bi is sufficient to produce the well know ductility loss at intermediate temperatures (see Fig. 1).

Despite its massive industrial application, segregation and transport data are mostly lacking for the Ni–Bi system. GB segregation was investigated using Auger electron spectroscopy by Chang and Huang [11]. However, reported segregation enthalpy exceeding 100 kJ/mol makes it worth to conduct complementing experiments to determine fundamental thermodynamic parameters using

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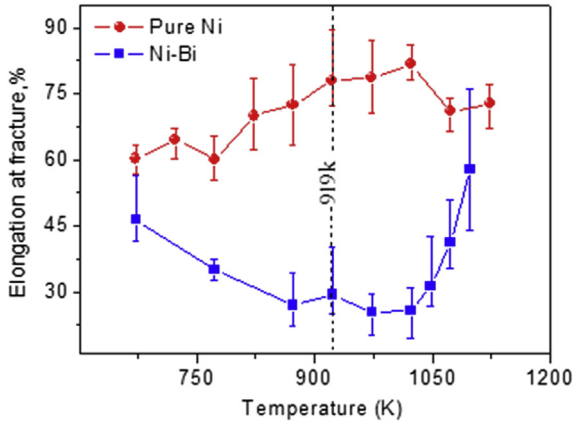

Fig. 1. Maximum elongation of high purity Ni and a Ni-25ppm-Bi alloy versus temperature of mechanical testing (Error bars display the maximum and minimum elongations of six samples with identical heat treatment and tension procedure). Maximum temperature (915 K) of stable intermetallic is indicated.

different, probably more accurate methods. Therefore in this article, we will present a study by atom probe tomography (APT) on GB segregation and related atomic transport in the Ni–Bi system. The instrument enables real three-dimensional chemical maps of the specimen in atomic resolution, which allows direct analysis of inclined GBs embedded into bulk volume. Individual atoms of the specimen are field-evaporated by short high voltage pulses, of up to 5 kV, superimposed on a constant bias voltage a few times larger than the pulse voltage itself. Evaporated atoms are accelerated towards a detector that records flight time and impact position. From data of detector events, the three-dimensional atomic arrangement of the specimen can be reconstructed with an accuracy of a few Angstroms [25]. As a decisive advantage, atom probe tomography does not require fracture of GBs to discover segregation. It allows direct local measurement of individual GB and to determine spatial distribution of the segregation zone.

2. Materials and methods

We investigated GBs of Ni-25wt ppm-Bi produced by vacuum induction melting, mixing high-purity Ni with the correct amount of high-purity Bi. The morphologies of the alloys were observed by scanning electron microscopy (SEM, FEI Nova 230 Nano). Furthermore, the samples were thinned to <100 nm thick with ZEISS CrossBeam 1540 EsB focussed ion beam system (FIB), lifted-out and cut by Gallium (Ga) ions. The atomic structure was performed by high-resolution transmission electron microscopy (HRTEM) model Zeiss Libra 200F.

Analysis was also carried out using a modern wide angle tomographic atom probe (WATAP). Base and pulse voltage are optimized for single atom detection (detection rate <0.05 atoms/pulse). The instrument is equipped with a 120 mm delay line detector and a flight length of 150 mm, which results in a numerical aperture of ±35°. Therefore, lateral size of the analyzed volume has been increased up to typically 100 nm in diameter. This allows measurement of rare defects with sufficient statistically significance [26,27]. Samples were evaporated by high voltage pulsing at a pulse rate of 20 kHz, a pulse fraction $U_{Pulse}/U_{DC} = 20\%$ and a specimen temperature of 80 K.

In order to obtain sufficient sample throughput for a kinetic study, which requires investigation of many samples in different reaction stages, we decided to deposit model layers on pre-shaped tungsten tips. Nanocrystalline ($Ni_{97}Bi_3$) alloy layers of about 25 nm thickness were deposited using a custom-built ion beam sputter device. An additional very thin Al layer was deposited on top of the coated specimens to avoid evaporation of Bi during subsequent heat treatments.

Coated tips were annealed in an ultra-high vacuum (UHV) furnace with a residual gas pressure below 1×10^{-7} mbar to induce Bi segregation to the grain boundaries. Annealing temperature was 623 K, annealing times varied from 15 to 120 min. The temperature of the tips inside the vacuum furnace was carefully calibrated against the melting point of high purity (99.998 wt%) Sn wires. Possible deviations between the measured and real temperatures of the nanometric tip are proven to be less than ±10 K in studied temperature regime.

Thin film deposition on curved substrates leads to significantly smaller grain size (in the range of 10 nm) in comparison to conventional industrial alloys. In order to compensate for the dramatically increased volume fraction of grain boundaries, the Bi content was increased to 3 at% in our model layers. This impurity content is certainly above the solubility limit for Bi in Ni [28]. As a decisive advantage, small grains improve the frequency of finding suitable GBs in the analyzed volume [29,30].

3. Results

Fig. 2(a) presents the SEM image of the binary Ni(Bi) alloy. Grains, GBs and triple junctions (TJ) are clearly seen. No intergranular precipitates in the size of submicrometers are shown. From the inset of the Fig. 2(a), the presence of a GB within the lamella can be identified by contrast of two grains. Fig. 2(b) shows TEM images of the lamella with emphasis on grain boundary as bright-field and high resolution electron microscopy (HREM) images respectively. No precipitation is formed at GBs.

Fig. 3(a) presents a mass spectrum obtained by APT-analysis of the sputter-deposited alloy layer with nominal 3 at% Bi in the as-prepared state. All major peaks are clearly identified and by virtue of their disparate atomic weights, no peak overlap is observed between Ni and Bi. Determined average concentration of Bi is close to the expected 3%, no systematic variation of the total Bi content is noticed with annealing time (see the table in the inset of Fig. 3(b)). Thus, potential Bi loss due to high vapor pressure is reliably prevented by Al coating.

Fig. 4 presents the compositional analysis of different annealing stages. Cross section through the atomic reconstruction and composition profile of the as prepared state (Fig. 4(a)) demonstrate a homogeneous Bi distribution. After annealing, enrichment of Bi at GBs of Ni is evident (see e.g. inset of Fig. 4(c). The complex 3D morphology of the GBs becomes nicely decorated by Bi markers. In order to analyze grain boundaries after annealing, local cylinders of analysis are oriented perpendicular to GBs and the corresponding concentration profiles are determined across the grain boundaries. Always, the cylinder orientation is optimized to reveal a chemical transition as sharp as possible, cylinder diameter was 6 nm. Examples of GB cross section profiles obtained after 15, 30 and 45 min annealing at 623 K are presented in Fig 4(b–d). Peak GB concentration reaches 9.8, 20.6 and 27.6 at% Bi, respectively. Also the width (w) of the segregation zone increases clearly with time.

Since width of segregation zones varies, it is obviously not sufficient to determine the peak composition to characterize the progress of segregation. A more robust parameter is the Gibbsian excess Γ that counts the number of additional Bi atoms per GB area. If tomographic reconstructions are evaluated in the vicinity to GBs, we frequently notice local density variations. Interestingly, we do observe increase of density as well as depletion. Until now, we could not identify an unambiguous correlation of this effect to grain orientation relation. In any case however, this density variation prevents simple determination of the Gibbsian excess from determined composition profiles. Instead, we generate ladder diagrams from the atomic data comprised in the analysis cylinder in the same way as