1. Introduction

The performance of engineering materials, especially the materials that are used in extreme/abnormal conditions viz., superalloys, superplastic, nanocrystalline or composite materials, depend critically on the properties of internal interfaces such as grain boundaries (GBs) and interphase boundaries (IBs). The behaviour of these interfaces (GBs and IBs) can alter the entire performance of the materials and under certain conditions leads to catastrophic failure [1,2].

GB embrittlement is one such most prominent phenomenon which is mainly caused by segregation of solute elements at GBs, which significantly degrades the performance of a polycrystalline material [3–5]. Grain boundary segregation of impurity/solute atoms occurs during the solidification or post-processing heat treatment because of their strong tendency to segregate. Irrespective of the very small amounts of these solute atoms (e.g., Bi, Sb, P, Sn, S, C), undesired embrittlement of metallurgical alloys frequently occurs [6]. The interfacial chemistry affects GB mobility, GB energy, and the stability of nanostructures [7,8]. The segregation of these solute elements along GBs may enhance the nucleation of second phases, creation of GB complexes [9], or even result in the localised melting of GBs [10,11].

The grain boundary embrittlement of Cu due to Bi segregation is a
well-known example and is investigated in detail [12–15]. Similarly, significant embrittlement in Ni-Bi alloys at 923 K and 1023 K was reported for the alloy with a 25 wt. ppm Bi content [16]. However, in-depth understanding of the Bi segregation behaviour and its influence on GB diffusion is lacking, which is imperative to control the technical performance of Ni-Bi alloys.

In their seminal work, Kikuchi and Cahn theoretically predicted the occurrence of a GB melting transition in a two-dimensional lattice-gas model [17,18]. It was shown that the GB becomes progressively more disordered (melted) with increasing temperature and the GB width diverges logarithmically at the melting point. According to the pre-wetting model [14], two thin quasi-liquid layers surround the GB in the Bi-rich GB phase, and the occurrence of a bilayer interfacial phase at grain boundaries in the Ni-Bi system was experimentally reported [19–21]. Even the formation of Bi segregation-induced superstructures along general grain boundaries has been observed [21]. Computer modelling suggests the formation of specific interfacial phases in the Ni-Bi system, too [22].

However, a direct experimental proof of the GB pre-melting transition, i.e., the appearance of a liquid-like GB layer in the Ni-Bi system is still missing. If a GB pre-melting phase transition does occur in the Ni-Bi system, it can be studied very sensitively in situ by specially designed radiotracer GB diffusion measurements [14]. The GB phase transformation and changes in the nature of the GB phases, especially if the formation of a liquid-like layer is involved, will manifest themselves in strong changes of the GB diffusivities. The latter can be studied with a high sensitivity, since the diffusivity depends exponentially on the corresponding changes in the interatomic interactions.

The present work investigates the segregation behaviour of Ni-Bi alloys in view of their vast industrial applications [23, 24]. The grain boundary diffusion of Ni in dilute polycrystalline Ni-Bi alloys is measured over wide temperature intervals in both B-type and C-type kinetic regimes using the radiotracer technique and applying the \(^{60}\)Ni radiisotope. The radiotracer measurements are combined with high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and atom probe tomography (APT) investigations. Utilizing the present experimental results, important insights are drawn into the GB phase transition and the GB pre-wetting phenomenon. A grain boundary diffusion map is proposed, explaining (correcting) the GB phase transitions with the variation of the Bi concentration.

2. Experimental procedure

2.1. Alloy preparation and characterization

The present diffusion/segregation study for the Ni-Bi alloys is focused on the solid solution (single phase) region of the equilibrium phase diagram. This is a very restrictive condition due to the low bulk solubility of Bi in solid Ni. Based on the available experimental data, Jiang et al. [22] constructed the Ni-Bi binary phase diagram utilizing CALPHAD approach. The phase diagram is shown in Fig. 1 using the logarithmic scale to highlight the Ni-rich corner [25].

Pure elemental pieces of nickel (3N8) and bismuth (5 N) were used to manufacture the Ni-Bi alloys. In view of Bi evaporation during melting, a master alloy of the Ni-3.8at.% Bi composition was prepared by induction melting, which was further used to prepare the Ni-Bi alloys for the current study. The Ni-Bi alloys containing 0.03, 0.07, 0.09, 0.14, 0.21, 0.23, 0.28 at.% Bi were prepared using vacuum arc re-melting. The elemental composition of the homogenised alloys were examined by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), Thermo Fisher Scientific ICAP 7500. The major impurities were found to be Ag (< 8 wt. ppm), Cr (< 5 wt. ppm), Co (< 6 wt. ppm), Mn (< 3 wt. ppm), Mo (< 3 wt. ppm) and Fe (< 10 wt. ppm each).

The manufactured Ni-Bi alloys were encapsulated in evacuated (5 × 10\(^{-5}\) mbar) quartz tubes after filling with high purity Ar (5 N) and were homogenized at 1373 K for 24 h. The homogenized ingots were cut into cylindrical discs of 8 mm diameter and 2 mm thickness by spark erosion and polished to a mirror like surface finish by standard metallographic polishing procedures. The polished discs were pre-diffusion annealed at 1373 K for 24 h to relieve the stresses on the samples surfaces that are induced during metallographic polishing.

The pre-diffusion annealed specimens were subsequently subjected to relaxation heat treatments at the temperatures of the respective tracer diffusion experiments for at least twice the time durations of the radiotracer experiments. This step allowed to establish an equilibrium segregation of Bi and the residual impurities and stabilize the grain size preventing GB motion during subsequent tracer diffusion experiments. The temperatures of the furnaces were well calibrated to an accuracy of ±1 K using a Ni-NiCr thermocouple. After each annealing the samples were quenched in water. To ensure adequate analysis and understanding of the grain boundary structures, identical heat treatment conditions were used for samples used both for tracer diffusion measurements and characterization.

The structural characterization of the processed samples was performed using X-ray diffraction (XRD, Siemens D5000) with Cu K\(_\alpha\) radiation (\(\lambda = 0.154\) nm) with an accelerating voltage of 40 kV and a current of 40 mA. The X-rays diffraction patterns were acquired at a step size of 0.02, a count time of 2 s per step using a diffractometer with the 0–20 geometry, and an area detection diffraction system. The microstructural characterisation was performed by scanning electron microscopy (SEM, FEI Nova 230 Nano), equipped with an electron back-scattered diffraction (EBSD) and energy dispersive X-ray spectroscopy (EDS). Furthermore, in-depth characterization of the selective samples was performed using a combination of transmission electron microscopy (TEM), HAADF-STEM and EDS to reveal the microstructural features and to accurately characterize the different segregation levels of Bi at the grain boundaries. To this end, a FEI Titan Themis 60–300 microscope was used with a high brightness field emission gun (X-FEG) operated at 300 kV acceleration voltage and 3.45 kV extraction voltage. The microscope was equipped with a monochromator, a quadrupole EDS system, a HAADF (Fischione Model 3000), and a fast CMOS camera (Ceta, 4k x 4k). Prior to TEM analysis, lamellae were cut from each alloy and thinned down to an electron transparent state using the focused ion beam (FIB) method with a ZEISS Crossbeam 340 microscope.

The thickness of the FIB lamella is maintained uniform, around
80–100 nm for all the samples to minimize the influence of the thickness on the STEM results. A Velox (Version: 3.5.0.952–085b33a529) software is used for the quantification of the STEM EDS results. Velox accounts for the sample thickness and density, for absorption correction as well as for density correction during the analysis which will result in a more accurate quantification.

Specimens for correlative microscopy by TEM and APT were prepared using a dual-beam SEM / FIB instrument (Scios, Thermofisher) via an in-situ lift-out protocol [26]. The regions of interest (high-angle grain boundary) were extracted from the bulk and subsequently attached to the electropolished tips of a halved TEM Mo-grid that was to be mounted in a special correlative holder designed in-house. The regions were sharpened by FIB milling at 30 kV followed by a final cleaning procedure at 2 kV and 16 pA current to remove severely damaged regions induced by previously by a high-energy Ga ion beam. Confirmation of presence of the grain boundary in the needle specimens were done using a TEM, Tecnai T20 operated at 200 kV.

Atomic-scale compositional analysis was performed by APT in LEAP-5000XHR (Cameca instruments) equipped with a reflectron. An ultraviolet picosecond pulse laser with a pulse repetition rate of 125 kHz and pulse energy of 55 pJ was used for field evaporation. The base temperature of needle specimens was maintained at 60 K with a target detection rate of 5 ions per 1000 pulses. The APT data analysis and reconstruction were performed using the IVAS TM 3.8.4 software package.

2.2. Grain boundary energy measurements

In order to measure the relative grain boundary energy, \( \gamma_{gb} / \gamma_s \), where \( \gamma_s \) is the surface energy and \( \gamma_{gb} \) is the grain boundary energy, a thermal grooving method in combination with atomic force microscopy (AFM) [27–29] was applied. The Ni-Bi alloys were first pre-annealed at 800 K for 48 h in purified Ar for the conditions mimicking the tracer diffusion experiments. Then, the samples were heat treated at 800 K for 24 h in the forming gas (Ar + 5 vol.% H\(_2\)) atmosphere for thermal grooving. The measurements of the GB groove dihedral angles were performed by atomic force microscopy (Park XE-100 AFM) operated in non-contact mode. AFM scans were performed with NSC15 ultra-sharp Al-coated Si tips with nominal radius of the tip curvature of 8 nm. GB groove profiles were taken from the AFM images after a routine flattening operation that enabled the calculation of the relative values of GB energy. Subsequently, the microstructural characterization of the investigated GBs was performed applying SEM analysis. The dihedral angle at the groove roots was measured and the results were averaged over 3 measurements for at least 10 GBs for a given alloy.

2.3. Radiotracer experiments

The \(^{63}\text{Ni}\) radioisotope (68 keV \( \beta \)-decays, half-life of 100 years) was available as a 0.5 M HCl solution. The original radiotracer solution was highly dissolved in double-distilled water to approach the intended specific radioactivity (about 5 kBq/\( \mu \)l). The diluted solution of \(^{63}\text{Ni}\) (about 10 kBq) was deposited on the polished surface of the sample and dried. The deposited samples were encapsulated in evacuated and then argon filled quartz tubes and diffusion annealed at the intended annealing conditions. After the diffusion annealing, the diameter of the samples was reduced by at least 1 mm to eliminate the influence of surface or lateral diffusion on the actual grain boundary diffusion profiles. The penetration profiles of the \(^{63}\text{Ni}\) isotope were determined by precision parallel sectioning via mechanical grinding. The thickness of each section was estimated by weighing the sample of known geometry before and after the grinding steps using a microbalance with a relative accuracy of 0.1 g. The activity of each section was determined using a Liquid Scintillation Counter (LSC, TRI-CARB 2500 TR). The obtained relative specific activity (normalized on the section mass) was plotted against the diffusion depth to determine the GB diffusivity.

3. Results and discussions

3.1. Microstructural characterization of the Ni-Bi alloys

A detailed knowledge of the alloy microstructure is essential for proper understanding of grain boundary diffusion. The phases present in the alloy and their distribution, nature of grain boundaries and the elemental segregation will directly influence the GB diffusion. The Ni-Bi alloys annealed at 1123 K for 24 h (and water-quenched) are found to feature single-phase face-centered cubic (FCC) structures as revealed by their XRD patterns shown in Fig. 2.

The micrographs in Fig. 3 reveal the particles of Bi-rich phase at GBs and GB triple junctions for the Ni-0.28 at.% Bi alloy. However, the amount of this phase is small and, therefore, the peaks of Bi-phase are not visible in the XRD patterns, Fig. 2.

Since all the alloys are processed under similar conditions, the microstructures (reasonably far from GBs) were found to be similar, except for the extent of Bi enrichment along grain boundaries and at triple junctions, especially in alloys with a higher Bi content. Fig. 3 presents a representative microstructural analysis for the Ni-0.28 at.% Bi alloy. Fig. 3(a) shows the back scattered electron image, which reveals the presence of a single phase (FCC) matrix and Bi-rich precipitates at GBs and triple junctions. The EBSD grain orientation map of the Ni-0.28 at.% Bi alloy with colour-coded GBs is shown in Fig. 3(b). The high-angle grain boundaries (HAGBs) are highlighted in black, and the low-angle grain boundaries (LAGBs) are marked by white line segments. It can be seen that the majority of grain boundaries are HAGBs with an average grain size in excess of 100 \( \mu \)m. This ensures ideal conditions for proper radiotracer diffusion measurements. The EDS analysis and the phase mapping shown in Figs. 3(c) and (d) confirm the presence of Bi-rich particles at GBs and a prominent Bi decoration of triple junctions. In Fig. 3(d), the black regions correspond to the FCC phase and the white regions are enriched with Bi which is in perfect agreement with the phase diagram presented in Fig. 1. Since these samples were annealed at 1123 K, the Bi-rich particles/regions correspond to the Bi melt which rapidly crystallizes by cooling. The composition of the Bi-rich regions was further analysed by APT, see Section 3.4 below.

In order to determine the characteristics of the GBs related to the different segregation levels of Bi at the grain boundaries, in-depth characterization of the grain boundaries was performed for the Ni-0.14 at.% Bi, Ni-0.21 at.% Bi, Ni-0.23 at.% Bi and Ni-0.28 at.% Bi alloys annealed at 1123 K for 24 h as well as after annealing at 650 K for 72 h. The variations in the segregation level of Bi along the grain

![Fig. 2. XRD patterns of Ni-Bi alloys annealed at 1123 K for 24 h showing the presence of a single-phase FCC structure.](image-url)
boundaries were investigated using HAADF-STEM combined with a four-quadrant EDS detector system. In general, the present tracer experiments were focused on the diffusion contribution of general (random) high-angle grain boundaries which constitute the fastest short-circuit paths in a polycrystalline material, see below. So, for a proper correlation of the structure analysis with the tracer diffusion measurements, general high-angle grain boundaries were selected for the preparation of STEM and APT specimens for further local in-depth characterization (STEM and APT). The grain boundary spectra for all alloys were first carefully examined using the EBSD analysis and the high-angle grain boundaries with almost the same misorientation parameters (typically, the misorientation angle $\theta = (45 \pm 5)^\circ$ and the misorientation axis of about $<011>$) were identified. Such boundaries were found to be present in almost all alloys and the FIB lamellae with those grain boundaries were then extracted. The specific misorientation parameters of all GBs for TEM and APT studies in the Ni-Bi system are listed in Table 1.

In the as-annealed condition, all the alloys are assumed to be in the single-phase solid solution region, as predicted by the phase diagram shown in Fig. 1. The presence of Bi particles in the Ni-0.28 at.%Bi alloy, Fig. 3, indicates that the CALPHAD diagram [22,25] (Fig. 1) does not fully represent the Bi solvus lines. This fact calls for a detailed study of Bi solubility in bulk Ni that is a subject of a separate study.

The left column in Fig. 4 shows the EBSD images of Ni-0.14 at.% Bi (a), Ni-0.21 at.%Bi (b), Ni-0.23 at.%Bi (c) and Ni-0.28 at.%Bi (d) alloys with emphasis on the grain boundaries. Figs. 4 (a-d) shows the EBSD patterns of the intended alloys for TEM analysis exhibiting HAGBs, and the positions of four selected lamellas are marked with the black open squares. From the EBSD analysis, exemplary shown in Fig. 4, it is found that all the samples are having a random texture which guarantees a reliable comparison of the GB diffusion properties with the variation in Bi content. Note that whereas bulk diffusion in Ni-Bi alloys is isotropic due to the cubic symmetry of the lattice, a certain anisotropy of GB diffusion in polycrystals may be expected [30]. However, the diffusion anisotropy of GB diffusion was found to relatively small, within a factor of two to three for purely tilt $\Sigma 5(310)[001]$ boundaries [31, 32] or even negligible for tilt $\Sigma 5(210)[001]$ GBs [31]. One might expect a less anisotropic diffusion behaviour for GBs with additional twist components, i.e. general high-angle GBs with a mixed character. Thus, we may safely expect a minimal/negligible influence of the almost random texture on the results of the present grain boundary diffusion measurements and compare reliably the results for different alloys.

Table 1
The misorientation parameters (axis and angle $\theta$) for the general (random) high-angle GBs selected for local (TEM and APT) studies in the Ni-Bi system.

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Misorientation parameters</th>
<th>the axis of misorientation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-0.14 at.% Bi</td>
<td>41°</td>
<td>&lt;1, 15, 3&gt;</td>
</tr>
<tr>
<td>Ni-0.21 at.% Bi</td>
<td>40°</td>
<td>&lt;27, 7, 2&gt;</td>
</tr>
<tr>
<td>Ni-0.23 at.% Bi</td>
<td>44°</td>
<td>&lt;12, 13, 1&gt;</td>
</tr>
<tr>
<td>Ni-0.28 at.% Bi</td>
<td>55°</td>
<td>&lt;72, 1, T&gt;</td>
</tr>
</tbody>
</table>

Fig. 3. A back-scattered electron (BSE) image showing a representative microstructure of Ni-0.28 at.% Bi alloy (a); the corresponding EBSD grain orientation map (colour-coded according to the inverse pole figure shown as insert) highlighting high angle grain boundaries (b); EDS mapping of Bi (c) and phase mapping (d). In (d), the black area correspond to the FCC phase and the white area is Bi, showing Bi-rich precipitation at grain boundaries and triple junctions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
Figs. 4(e-p) represent the example of high-angle annular dark-field (HAADF) images, corresponding EDS maps and selected line scan results of grain boundaries that are relevant to analyse the tracer diffusion results. The HAADF-STEM images substantiate the segregation of Bi in the Ni-Bi alloys annealed at 1123 K for 24 h. A substantial increment of the Bi segregation layer thickness along the grain boundaries with the increment in the Bi concentration is observed. These features of grain boundary segregation turned out to be critical for the analysis of the measured diffusion profiles since different levels of Bi segregation affect the short-circuit diffusion paths and their contribution has been carefully evaluated (see Section 3.2).

3.2. Ni GB diffusion in Ni-Bi alloys

Grain boundary diffusion of the $^{63}$Ni radioisotope in Ni-Bi alloys is measured over wide temperature intervals using the radiotracer technique in Harrison’s [33] B- and C-type kinetic regimes. The experimental conditions (temperatures and alloy compositions) are sketched in Fig. 1.

By performing GB diffusion experiments in Harrison’s both B- and C-type kinetic regimes [33] on the same polycrystalline material, one determines fundamentally different kinetic quantities [34]. In the C-type regime, the tracer atoms will diffuse almost exclusively along the GBs without a leakage to the adjacent bulk crystals and the GB diffusion coefficients, $D_{gb}$, can directly be measured. In contrast, in the B-type regime the bulk diffusion length, $\overline{D_v t}$, is significantly larger than the GB width $\delta$ and far from the external surface the bulk tracer concentration is exclusively determined by out-diffusion of the solute tracer from the GBs to the bulk ($D_v$ and $t$ are the bulk diffusion coefficient and the diffusion time, respectively) [35].

The resulting amount of the tracer atoms in the bulk therefore depends on the ratio between the tracer concentrations in the GB, $c_{gb}$, and in the adjacent bulk layer, $c_v$, i.e., on the GB segregation factor $s = c_{gb}/c_v$ (see e.g. [35]). Thus, only the so-called triple product $P = s D_{gb} \delta$, where $\delta$ and $D_{gb}$ are the GB width and GB diffusion coefficients, respectively, can be determined from GB diffusion experiment in the B-type kinetic regime [33]. The average GB width $\delta$ can in turn be determined by the combination of the B- and C-type regime measurements for GB self-diffusion in a pure metal (then the segregation factor $s$
values of the Le Claire parameters $\alpha$, Eq. (1), and $\beta$, Eq. (2) [39]. The parameter $\alpha$ represents the ratio of the effective GB width, $s_\delta$, and the volume diffusion length, $\sqrt{Dv_t}$,

$$\alpha = \frac{s_\delta}{2\sqrt{Dv_t}}$$  \hspace{1cm} (1)$$

It is well known that the GBs provide short-circuit diffusion paths and facilitate accelerated diffusion of tracer atoms. The diffusion occurs into the grain interior (bulk or volume diffusion), too, which is comparatively slower process.

The parameter $\alpha$ determines the possible leakage of the tracer atoms from GBs into the grain interiors by bulk/volume diffusion. Typical values of $\alpha$ in the true C-type kinetic regime satisfy $\alpha \geq 1$ and for the B-type kinetic regime, values of $\alpha < 0.1$ are accepted [39]. Grain boundary diffusion in the B-type kinetic regime is also described by the parameter $\beta$, which determines the high temperature limit for these measurements when the GB contribution could be discriminated from direct volume diffusion,

$$\beta = \frac{D_{gb}}{D_v} \frac{P}{2D_v^{3/2}}$$  \hspace{1cm} (2)$$

It is generally accepted that the value of $\beta$ has to be sufficiently large (typically $\beta > 10$ [39]). Here, $s$ is the solute segregation factor (for self-diffusion $s = 1$), $t$ is the diffusion time, $D_v$ is the bulk diffusion coefficient, $P$ is the triple product. It is assumed also that $D_{gb}/D_v > 1$.

In order to determine the diffusion parameters $\alpha$, $\beta$ and the triple product $P$ for the B-type kinetic diffusion regime, the bulk diffusion ($D_v$) coefficient of Ni has to be known. The $D_v$-data of Maier et al. [40] were used in the present work,

$$D_v = 9.2 \times 10^{-3} \exp\left(\frac{-278 \text{ kJ mol}^{-1}}{RT}\right) \text{m}^2 \text{s}^{-1}$$  \hspace{1cm} (3)$$

Here $R$ denote the universal gas constant.

In the present study, we will assume that the Ni diffusion rates in the crystalline bulk of the Ni-Bi alloys are not strongly affected by the dissolved Bi atoms due to their low concentration. According to the Lifshitz theory [41], the solvent enhancement factor is between 0 and 100 for crystalline bulk of the Ni-Bi alloys are not strongly affected by the dissolved Bi atoms due to their low concentration. The corresponding corrections are relatively small in the present conditions.

3.2.2. The C-type regime of GB diffusion

The C-type kinetic conditions are usually satisfied at low temperatures and short diffusion times, where diffusion in the bulk is negligible, and the diffusional transport proceeds solely along grain boundaries. Therefore, the GB contribution branches of the penetration profiles are mainly considered for the current study. The corresponding branches of the penetration profiles are fitted using appropriate mathematical solutions and are shown as solid lines in the figure. The relevant - experimental parameters (diffusion annealing temperatures $T$, annealing time $t$, bulk diffusion length and $\alpha$) are listed in Table 2. For the estimation, a segregation factor for Ni of about unity is assumed. The determined triple products ($P$) and $\beta$ of all the diffusion measurements performed in the temperature interval from 800 to 1223 K are given in Table 3.

At $T = 800 \text{ K}$, the kinetic conditions of the B-type regime were almost fulfilled, since $\alpha = 0.16$, see Table 2. Strictly speaking, the experiments with $0.1 < \alpha < 1$ belong to the transition regime between the B-type and C-type kinetics [33] and the derived data can be corrected using the approach suggested by Szabo et al. [45]. An analysis showed however that the corresponding corrections are relatively small in the present case and are below the uncertainties of the determined triple product values. For this reason, the corrections were not performed.

3.2.2. The C-type regime of GB diffusion

The C-type kinetic conditions are usually satisfied at low temperatures and short diffusion times, where diffusion in the bulk is negligible, and the diffusional transport proceeds solely along grain boundaries. These conditions correspond to $\alpha > 1$ and the grain boundary diffusion coefficient, $D_{gb}$ can directly be determined from the penetration profile. If the Gaussian solution is applied, $D_{gb}$ is proportional to the slope of the penetration profile in the ln$C$ vs $y^2$ coordinates,

$$D_{gb} = -\frac{1}{4t} \left(\frac{\partial\ln C}{\partial y^2}\right)^{-1}$$  \hspace{1cm} (5)$$

Here $t$ and $y$ are the tracer concentration and the penetration depth, respectively.

The penetration profiles of $^{63}\text{Ni}$ measured in the C-type kinetic regime at 650 K in the Ni-Bi alloys are shown in Fig. 6. After an initial decrease of the tracer activity by more than two orders of magnitude (related to remnant surface activity and grinding-in effects), a prolonged tail corresponding to GB diffusion is measured and it is almost linear with respect to depth squared, $y^2$. For the depths below about 10–15 μm, two distinct branches, which are linear in the given coordinates, are resolved (only one such branch exists for pure Ni), Fig. 6(a). The linear branches of the penetration profiles allow reliable determination of the GB diffusion coefficients, $D_{gb}$, via Eq. (5).

Generally, it is extremely difficult to decide about the diffusion kinetics solely from the shape of the concentration profiles (e.g., linearity against $y^6/5$ or $y^2$ for instantaneous source conditions). In the present work, the different diffusion regimes were classified according to the values of the parameter $\alpha$ that are presented in Table 2.

In the Bi containing Ni-Bi alloys, two distinct short-circuit contributions in the penetration profiles are observed even at depths larger

$\beta = 1$ and the experimental data confirms that the diffusional GB width $\delta$ is about 0.5 nm [36–38].

The penetration profiles for GB diffusion in the B- and C-type regimes have to be processed differently and the classification is based on the values of the parameters $\alpha$ and $\beta$.

### Table 3

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{gb}$</td>
<td>1.308 x 10^{-3} \exp\left(\frac{-278 \text{ kJ mol}^{-1}}{RT}\right) \text{m}^2 \text{s}^{-1}$$</td>
</tr>
</tbody>
</table>
Table 2
The parameters (annealing temperature T and time t) of the $^{63}$Ni radiotracer GB diffusion experiments. At 800 K, the B-type conditions are almost fulfilled (marked by a star).

<table>
<thead>
<tr>
<th>T (K)</th>
<th>t ($10^3$ s)</th>
<th>$\sqrt{D_{3T}}$ (µm)</th>
<th>α</th>
<th>Regime</th>
</tr>
</thead>
<tbody>
<tr>
<td>1223</td>
<td>0.18</td>
<td>1.49</td>
<td>1.88 x 10^{-4}</td>
<td>B</td>
</tr>
<tr>
<td>1173</td>
<td>0.252</td>
<td>0.98</td>
<td>3.01 x 10^{-3}</td>
<td>B</td>
</tr>
<tr>
<td>1123</td>
<td>0.84</td>
<td>0.96</td>
<td>2.59 x 10^{-3}</td>
<td>B</td>
</tr>
<tr>
<td>1023</td>
<td>0.84</td>
<td>0.23</td>
<td>1.11 x 10^{-3}</td>
<td>B</td>
</tr>
<tr>
<td>800</td>
<td>0.36</td>
<td>0.0015</td>
<td>1.64 x 10^{-1}</td>
<td>B*</td>
</tr>
<tr>
<td>650</td>
<td>2.592</td>
<td>0.033</td>
<td>7.58</td>
<td>C</td>
</tr>
</tbody>
</table>

Table 3
The determined GB diffusivities, P, (in m²/s) of the $^{63}$Ni radiotracer in the B-type regime in the Ni-Bi alloys. The values of the parameter $\beta$, Eq. (2), are listed, too.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$\beta$ ($10^5$)</th>
<th>P ($10^{-2}$)</th>
<th>Bi content (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>1.10</td>
<td>2.17</td>
<td>0.03</td>
</tr>
<tr>
<td>1023</td>
<td>2.14</td>
<td>3.21</td>
<td>0.09</td>
</tr>
<tr>
<td>1123</td>
<td>2.13</td>
<td>3.22</td>
<td>0.33</td>
</tr>
<tr>
<td>1173</td>
<td>2.16</td>
<td>3.26</td>
<td>0.89</td>
</tr>
<tr>
<td>1223</td>
<td>2.17</td>
<td>3.22</td>
<td>0.03</td>
</tr>
</tbody>
</table>

parallel (not sequentially), since the penetration depths are smaller than the average grain size. While their contributions are seen at different depths (the contribution of “fast” GBs is masked by the “slow” GBs at low depths), one may have an impression that “slow” interfaces are located near the sample surface and “faster” ones are found in the sample interior. Definitely, a homogeneous distribution of these two shortcircuit types is considered in the analysis.

Thus, within the expected experimental limitations, it can be concluded that at least two distinct short circuit fluxes with significantly different diffusion coefficients appear in the Ni-Bi alloy during annealing at 650 K and such paths are absent in pure Ni. The experimental parameters and the determined diffusion coefficients of the two different diffusion paths are listed in Table 4.

3.3. Composition dependence of Ni GB diffusion in Ni-Bi alloys

The concentration dependence of the triple products, P, of Ni diffusion in the Ni-Bi alloys is shown in Fig. 7(a). Accounting for concentration-dependent enhancement factors of GB diffusion, $b(x_B)$,

$$b(x_B) = \frac{\partial P(x_B)}{\partial x_B}$$


three regions could be distinguished, schematically separated by dashed lines in Fig. 7 (here $x_B$ is the nominal Bi concentration in the Ni-Bi alloys). As an example, the values measured at T = 800 K are shown in Fig. 7(b) separately. The three regions of the concentration dependence
of P(xBi) features basically different values of the enhancement factors \( b \) (note that we are nominally in the same single-phase solid solution region of the bulk phase diagram, Fig. 1):

Table 4
The determined GB diffusivities of \(^{63}\)Ni radiotracer at \( T = 650 \) K in the C-type regime for slow (\( D_{gb}^S \)) and fast (\( D_{gb}^F \)) branches.

<table>
<thead>
<tr>
<th>Bi content (at.%)</th>
<th>( D_{gb}^S (m^2/s) )</th>
<th>( D_{gb}^F (m^2/s) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>–</td>
<td>3.35 ( \times 10^{-15} )</td>
</tr>
<tr>
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Region I: \( (x_{Bi} \leq 0.1 \text{ at.%Bi}) \) The enhancement factor for GB self-diffusion of Ni is very moderate, the Ni diffusivity increases only slightly with increasing Bi concentration \( x_{Bi} \), remaining almost unchanged and equal to that for Ni GB diffusion in pure Ni.

Region II: \( (0.1 \text{ at.%Bi} < x_{Bi} \leq 0.25 \text{ at.%Bi}) \) A sudden enhancement of Ni diffusivity is prominent, corresponding to large values of the enhancement factor \( b \). Small changes of the Bi concentration, \( x_{Bi} \), result in large changes of the triple product \( P \).

Region III: \( (x_{Bi} > 0.25 \text{ at.%Bi}) \) The rate of increase of the Ni diffusivity is significantly decreased, corresponding to relatively small values of the parameter \( b \).

The limiting Bi concentrations are specified for the temperature of 800 K.

At the lowest temperature at which diffusion measurements was carried out in the present study, \( T = 650 \) K, only Regions II and III could unambiguously be resolved, see Fig. 8. The Region I corresponds likely to very small Bi concentrations which were not accessible in the present

Fig. 6. Penetration profiles of Ni GB diffusion in Ni-Bi alloys measured at 650 K in the C-type kinetic regime. (a) all profiles obtained in the C-type kinetic regime (b) diffusion profiles of pure Ni, and the lowest and highest composition of Bi in this work. The derived values of \( D_{gb} \) from the respective profile sections are also indicated.

Fig. 7. Concentration dependence of the triple product \( P \) of Ni GB diffusion in the Ni-Bi alloys at five different temperatures (a). In (b), a magnified representation of the data measured at \( T = 800 \) K is shown, the red open circles represent the diffusivity of pure Ni. Three distinct regions with different concentration dependence of the Ni GB diffusivity are indicated (see text). The inset images are the corresponding EDS maps of Bi in three different Ni-Bi alloys. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
investigation. Again, the Ni diffusion coefficient increases rapidly in Region II and the increase becomes moderate in Region III for \( x_{\text{Bi}} > 0.05 \) at.% Bi. Note that at this temperature, the three alloys with the highest Bi concentrations correspond to the two-phase region, FCC Ni(Bi) solid solution + NiBi.

As it was mentioned above, two different diffusivities were determined from the concentration profiles in the C-type regime. In Fig. 8, the filled black symbols correspond to the measured values of \( D_{\text{F}}^{gb} \), and the open red circles correspond to the measured values of \( D_{\text{S}}^{gb} \). While the values of \( D_{\text{F}}^{gb} \) increase significantly compared to the GB self-diffusion coefficients for Ni in pure Ni, the slow branch reveals almost constant diffusivities similar to those for Ni GB diffusion in pure Ni.

Note that the measured Ni GB diffusion coefficients in pure Ni correspond to the contribution of general (random) high-angle GBs and represent the fastest GB diffusion rates observed in well-annealed polycrystalline material \([36,37]\). With addition of Bi to Ni, even higher diffusivities are consistently measured. Still we conclude that at least in the alloys with a Bi content below 0.3 at.%, some fraction of general high-angle GBs remains almost free of segregated Bi atoms featuring the diffusion rates similar to those in pure Ni, Fig. 8. Thus, the present data support a strong (and probably intrinsic) heterogeneity of Bi segregation at general high-angle GBs in polycrystalline nickel. A similar behaviour has previously been observed for Cu-Bi alloys, too \([15]\). The heterogeneity of Bi segregation is probably related to a heterogeneous distribution of grain boundary defects (dislocations \([46,47]\), dislocation networks \([48]\), disconnections \([49]\), nano-faceting \([19]\)) which affect strongly the local segregation tendency of interfaces.

### 3.4. Heterogeneity of grain boundary structures in Ni-Bi alloys

Fig. 8 indicates the presence of different types of high-angle GBs with different segregation levels of Bi, which could be responsible for the two different diffusivities measured in the C-type kinetic regime. Therefore, a correlative analysis of atomistic structure (TEM) and diffusivity (radiotracer technique) has been performed on a Ni-0.28 at.% Bi alloy annealed at 650 K for 72 h. This annealing treatment mimics the
conditions for the C-type diffusion measurements. Fig. 9(a) shows the HAADF-STEM image of a selected region of interest, i.e. a high-angle grain boundary, and the corresponding EDS maps of Bi are shown in Fig. 9(b). They manifest heterogeneity of Bi segregation along GBs. After annealing at 650 K for 72 h, there is still the “clean” part of a GB without any observable segregation, Fig. 9(d). Crossing the “clean” part of the GB, the line scan (Line1) reveals a uniform distribution of Bi and the absence of segregation is seen, Fig. 9(c). However, at an adjacent location of the same GB, a strong localised enrichment of Bi is observed (Line2) and the Bi concentration is increasing significantly, from 0.25 at. % within the grain interior up to about 2.5 at. % at the GB, as shown in Fig. 9(d). Note that the diffusion measurements indicate the presence of both “clean” and well as Bi-enriched GBs in the alloys, Fig. 8.

The heterogeneity of Bi coverage of GBs was confirmed by APT study. In Fig. 10, the results of the APT measurements for the Ni-0.28at.% Bi alloy are presented. Regions with a Bi-enriched/segregated high-angle grain boundary were selected for the APT sample preparation. A suitable high-angle GB was carefully chosen by SEM inspection and a tip was lifted, see left panel in Fig. 10. Bright-field TEM image confirms the presence of the GB in the extracted tip (central panel in Fig. 10).

The APT reconstruction image shown in Fig. 10 (central panel) represents one side of the grain boundary with a Bi-rich precipitate which confirms the strong heterogeneity of Bi distribution along the inspected GB in the Ni-0.28at.% Bi alloy. The Bi concentration reaches about 90 at.% in the particle, see the proximity histogram [50], right panel in Fig. 10. The thickness of the Bi-rich precipitate is about 10 nm in the specified area. Thus, both nanometre- as well as micrometre-large Bi-rich precipitates (e.g., with a bright contrast in Fig. 10, left panel) co-exist with the Bi segregation layers at the high-angle grain boundaries in the Ni-0.28at.% Bi alloy.

3.5. Structure-diffusivity correlation for GBs in Ni-Bi alloys

In this work, the Ni GB diffusion rates in a series of Ni-Bi alloys in the temperature range of 650–1223 K are measured. In Fig. 11, the measured diffusivities, $D_{\text{Bi}}^{\text{Ni}}$, are normalized on the corresponding values for Ni diffusion in pure Ni, $D_{\text{Ni}}^{\text{Ni}}$. A conspicuous enhancement of Ni diffusivity by more than one order of magnitude is observed at all five temperatures.

The present experimental datasets indicate a series of Bi-induced GB phase transitions within the single phase Ni(Bi) solid solution area of the bulk phase diagram. The situation is fundamentally different from that for Cu-Bi alloys where a single and steep increase of the GB diffusion rates was related to the GB pre-melting phase transition [15]. In case of the Ni-Bi alloys, the GB diffusivities are systematically increasing with the increment in Bi content (however with remarkably different values of the concentration-dependant enhancement factors, $b(x_B)$), see Eq. (6) from Region I to Region II and to Region III as depicted in Figs. 7 and 8.

Note that the values of the triple product for Ni GB diffusivities, $F = \delta D_{\text{Bi}}$, measured in Region III at the highest temperatures are about $10^{-18}$ m$^2$/s, Fig. 7. Assuming the absence of a (strong) Ni segregation to the GBs in these alloys and taking the GB width of about 1 nm, these values of the triple product are translating to values of the GB diffusion coefficients of about $10^{-2}$ m$^2$/s. These are values typical for diffusion in melts.

Moreover, the triple product values measured for the compositions belonging to Region III are found to be almost equal within the typical experimental uncertainties, although one might speculate about an increasing trend of the diffusivity. We anticipate that because of the presence of wetting/pre-wetting films either with wetting by a liquid Bi-rich phase at $>960$ K or by the B2 NiBi phase, thus a solid phase wetting/prewetting [51] in the Regime III, the diffusivity is quite fast in all the compositions falling in Region III. Thus, our data allow the conclusions on the existence of a wetting/pre-wetting GB phase transition in the Ni-Bi system (Region III) and, therefore, on the existence of liquid-like GB layers for the corresponding Bi contents in the alloys, i.e. between the bulk and GB solidus lines in this system.

An enhancement of GB diffusion via the formation of wetting/pre-wetting layers is well known to be used in the process of “activated sintering” [49, 50]. Classical theories of multiple interfacial phases at GBs recognize the existence of three distinct interfacial phases at GBs: intrinsic (clean) GBs, Langmuir-McLean (L-M) monolayer, and complete GB wetting/pre-wetting film [19]. In terms of GB complexities and complexion transitions, bilayer and multi-layer are further distinguished [52].

High-resolution transmission electron microscopy (HRTEM) micrographs revealed four distinct interfacial phases in the Ni-Bi alloys annealed at 1123 K for 24 h, Fig. 12c: classical Bi segregation in Ni-0.14 at.%Bi (a), bilayer and tri-layer adsorption in Ni-0.21at.%Bi (b), multilayer adsorption in Ni-0.23at.%Bi (c), and an intergranular film in Ni-0.28at.%Bi (d). In the present work, at least two different grain boundaries in each alloy were examined and found to have perfect agreement with the GB phases that are already reported for Ni-Bi alloys [19–21]. Due to the strong agreement with the existing literature, the present results are used to analyse correlations between kinetic and microscopic results.

In the present work, for the first time a serial transition between the different GB phases, intrinsically correlated with the changes of the GB diffusion rates, is demonstrated. Moreover, in the Ni-0.21 at.%Bi alloy, the Bi segregation is found to be non-uniform and changes between bi- and triple-layer adsorption occurred along the same interface, see Fig. 12e.

The conventional Ni-Bi phase diagram cannot explain the sequence of GB phase transitions. The present results are used to construct a grain boundary diffusion map for the Ni-Bi system for general high-angle GBs. In the figure the overlaid orange dotted line indicates the first-order GB.
Fig. 11. 3D-plot of the concentration dependence of the relative Ni GB diffusivity, $P_{(Ni-Bi)}/P_{(Ni)}$, of the Ni-Bi alloys. The full symbols correspond to the measured triple product values. The purple area represents Region I, "clean GBs", the green area represents Region II, the GB transition zone, and the yellow area is Region III, the wetting/pre-wetting phase area. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 12. Examples of grain boundary phases observed in Ni-0.14 at.%Bi (a), Ni-0.21 at.%Bi (b), Ni-0.23 at.%Bi (c) and Ni-0.28 at.%Bi (d) alloys after annealing at 1123 K for 24 h. With an increasing Bi content in the Ni-Bi alloys, successive transitions occur from common segregation (a), double and triple layer segregation (b), multi-layer segregation (c) and finally to a liquid-like film (d). At the same time, a characteristic transition between double- and triple-layer segregation along the same GB is found for the Ni-0.21 at.%Bi alloy (e).
transition in the GB phase diagram proposed by Zhou et al. [25]. In Fig. 13, this GB transition line is further improvised using the extensive analysis of the present GB diffusion measurements and the direct HRTEM examinations (at 1123 K) presented in Fig. 12. Since the present study provides the structural characterization at a single temperature of 1123 K, the GB diffusion map can be transformed to GB phase diagram at 1123 K. With the detailed structural characterization of Bi-rich GBs at various temperatures one may verify the entire GB phase diagram which can be of interest for a future study. However, due to a limited structural information, the GB diffusion map is well defined in the context of the present GB diffusion measurements.

This is explained by a high sensitivity of GB diffusion measurements to even small variations in the composition. Even small variations of the atomic structure, causing probably correspondingly small changes of the grain boundary energy, induce an exponential response of the diffusion rates. This is why the grain boundary diffusion measurements provide the most sensitive probe of the structural changes in a sample.

Based on the analysis of the diffusion results, distinct regions can be identified for the distinct GB phases; corresponding GB phase transitions in the Ni-Bi GB diffusion map are presented by the dashed lines in Fig. 13. Using the structure information at 1123 K, the existence of three distinct regions of the concentration dependence of Ni GB diffusion (Section 3.3) are explained in terms of a sequence of GB phase transitions. At a specific temperature $T_0 = 1123$ K, with an increasing Bi concentration in the Ni-Bi alloys, the following transformations occur:

**Region I** represents a single solid solution phase, with ‘clean’ or ‘bare’ GBs and segregation of Bi atoms, see the scheme in the left-upper panel in Fig. 13. In this region, the change of the Ni GB diffusivity with addition of Bi is measurable, but small, i.e. the corresponding enhancement factor $b$, Eq. (6), is relatively low.

**Region II** corresponds to a transition to bi-layer and further to multi-layer Bi segregation. The schemes at the bottom-left and upper-right panels in Fig. 13 indicate the corresponding atomic configurations at the GB. The Ni diffusivities are increasing significantly with an increase of the Bi content, corresponding to large values of the factor $b$, Eq. (6). Fig. 12(e) suggests a continuous transition from bi- to three-layer Bi segregation with increasing Bi content as thickening of the Bi segregated layer.

**Region III** corresponds to the presence of a pre-wetting layer. By exceeding the GB solidus concentration, GB diffusivities becomes significantly enhanced with respect to the diffusivities in pure Ni and the further enhancement with Bi concentration is again moderate, corresponding to the thickening of the liquid-like GB layer, Fig. 12(d) and bottom-right panel in Fig. 13.

Having determined the triple product values, $P = s_0 D_{gb}$ and having performed atomic scale structure and chemical analyses, one may think to decompose the triple product into separate contributions and estimate the Ni diffusion coefficient, $D_{gb}$. However, one has to differentiate the “diffusional” GB width (as it is entering the GB diffusion problem [53]), the “structural” GB width (as it can be determined by TEM or APT) or “segregation” GB width (as determined by chemical analysis) which represent generally different quantities [54]. The diffusional GB width corresponds to the width of the layer with orders-of-magnitude enhanced diffusivities with respect to those in the bulk. There is no abrupt transition from slow (bulk) diffusion to high (GB) diffusion with approaching the exact interface position, as it is assumed in a simple Fisher model [55] in which a grain boundary is represented by a homogeneous slab. Nevertheless, an accurate analysis of GB diffusion in the B-type kinetic regime accounting for some transversal distribution of the GB diffusion coefficients as a function of the distance to the GB plane confirmed the correctness of the analysis in terms of the Fisher model and the product $P = s_0 D_{gb}$ (clearly defined for a GB slab) has to be considered as a product of effective values [55]. That analysis has been performed for self-diffusion, i.e. for the absence of GB segregation.

In the case of a strongly segregating solute, the situation becomes more complicated. One may have a segregated layer of a thickness of several nanometers where the solute atoms replace the matrix atoms without any disturbance of the GB structure. This is, e.g., the case of Ga in Al, where up to 3 monolayer of Ga atoms might be found at Al grain boundaries and the structure remains unchanged [56]. If one would perform a tracer diffusion experiment with a solute in such a case, one will measure the product $P = s_0 D_{gb}$ (as an effective value) but it is not trivial to decompose the product. One may argue that the diffusional
(effective) GB width will remain unchanged (about 0.5 nm) although a thicker segregated GB layer will be present. As an effective segregation factor, one might have to consider the ratio of the rates of atom exchanges between the GB core and the next crystalline layer (still within the segregated layer). It is not trivial to determine both these values, i.e. δ and s, by a local technique like TEM. Furthermore, one has to distinguish the segregation factor s (again, as it is entering the GB diffusion problem [53]) and the enrichment factor b or GB excess Γ (as they are provided by the local chemical analyses [57]), see e.g. Ref. [58].

3.6. Temperature dependence of Ni GB diffusion in Ni-Bi alloys

In Fig. 14, the measured Ni GB diffusivities, i.e. the triple product values, \( P \) (symbols), are compared with the most reliable literature data [37,59-61] (different type of lines). Furthermore, in the present investigation, GB self-diffusion in pure Ni was measured in the C-type kinetic regime as well and the determined GB diffusion coefficient is shown, too (right ordinate axis). As a result, the diffusional GB width, \( \delta \), was determined to be 0.64 ± 0.02 nm. This value agrees with the results of previous measurements [37,59-61], which suggests that the commonly accepted value, \( \delta = 0.5 \) nm, is a good estimate and can be used in GB diffusion theories and applications.

The Arrhenius parameters of Ni GB diffusion in Ni-Bi alloys were determined for the temperature intervals located in the same region of the constructed GB diffusion map, Fig. 13, and the results are listed in Table 5. For the alloys with lower Bi contents, between 0.03 and 0.09 at. % Bi, the GB diffusivities follow almost perfect Arrhenius dependencies in the temperature ranges from 800 K to 1223 K. However, two different slopes are required when fitting the P-values for Ni-0.14 at.% Bi alloys, which could be explained by residing in two distinct regions of GB segregation with varying annealing temperature. As for the alloy with higher contents of Bi, from 0.21 to 0.28 at.% Bi, the samples belong to a single region of GB segregation. With the annealing temperatures changed from 800 to 1223 K, all the Ni-0.21 at.% Bi and Ni-0.23 at.% Bi alloys are in the Region II, the Ni-0.28 at.% Bi alloys is in Region III.

3.7. Grain boundary energy

Figs. 4(g) and (k) demonstrate the case of so-called complete wetting/pre-wetting of a GB by the Bi-rich melt (which solidifies during quenching). In this case the contact angle between the GB and the two alloy/precipitate interfaces tends to zero. The precipitates continue into Ni/Ni as a pre-melting multilayer Bi-rich segregation film. Figs. 4(h) and (l) indicate another specific configuration at a triple junction composed by a GB with a strong Bi segregation and two alloy/Bi precipitate interfaces. The contact angle in this case is non-zero like in case of incomplete (partial) GB wetting. However, in case of true incomplete wetting, the precipitate contacts “clean” GB with only weak segregation (below one monolayer). Figs. 4(h) and (l) substantiate that the Bi-rich precipitate contacts the GB with several nm thick film of multilayer segregation (according to the APT data, Fig. 10, the thickness of the Bi layer varies between 10 and 30 nm). This case is called pseudo-incomplete (or pseudo-partial) GB wetting [62]. The pseudo-partial

![Fig. 14. Arrhenius diagram for Ni GB diffusivity in Ni measured in this work (red squares) in comparison to the literature data measured by Divinski et al. [37], Bokstein et al. [59], Frank et al. [60] and Rothova et al. [61]. The estimation of the GB width \( \delta \) is sketched. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)](image-url)
GB wetting has been observed previously in WC-Co [63], Al-Zn [64] and Nd-Fe-B [65] alloys. We may estimate the ratio of GB energy, $\gamma_{gb}$, to the energy of matrix/precipitate interface, $\gamma_{mp}$, as $\frac{\gamma_{gb}}{\gamma_{mp}} = 2\cos(\Psi/2)$, where $\Psi$ is the above-mentioned angle between the two alloy/Bi precipitate interfaces. For the Ni-0.21 at.% Bi and Ni-0.28 at.% Bi alloys, the angles $\Psi$ are measured to be equal to 10.8° and 72.2° that translates to the energy ratios of 1.99 and 1.62, respectively.

Furthermore, in the present work the thermal grooving method [27–29] and AFM characterization were applied to determine the grain boundary energies of the Ni-Bi alloys (in fact, the ratio of the grain boundary energy, $\gamma_{gb}$, and the surface energy, $\gamma_{s}$). For this aim, the samples were annealed at 800 K for 24 h in forming gas (Ar + 5% H₂) atmosphere.

The conventional method for measuring the GB energy is based on the geometry of the equilibrium thermal groove being formed at the intersection of the GB plane with the free surface. Under the assumption of full surface isotropy, the ratio $\frac{\gamma_{gb}}{\gamma_{s}}$ is determined employing Mullins’ relationship [66]:

$$\frac{\gamma_{gb}}{\gamma_{s}} = 2\cos\left(\frac{\theta}{2}\right)$$

where $\theta$ is the dihedral angle at the root of the GB groove, see Fig. 15 below.

In the temperature range of the present measurements, the surface diffusion coefficient, $D_s$, can be estimated as [67],

$$D_s = 1.4 \times 10^{-5} \exp\left(\frac{-7 \times T_m}{T}\right) m^2 s^{-1}. \quad (8)$$

This relation has been suggested for FCC metals [67] and it yields surface diffusion lengths of more than 200 μm for the present annealing conditions, which are much larger than the average groove width (less than 1 μm). Therefore, it follows that the dihedral angles obtained in these samples correspond to a full mechanical equilibrium established at the roots of the GB thermal grooves and Eq. (7) can be used.

Employing the analysis of Saylor and Rohrer [68], the instrumental AFM errors in determining of the relative GB energy are found to be negligible. As an example, the SEM micrographs of pure Ni and Ni-0.28 at.% Bi alloy, after annealing at 800 K for 24 h are presented in Fig. 15(a) and (b), respectively. The 3D AFM images of two typical GB grooves are shown in Fig. 15(c) and (d), and the corresponding linear topography profiles (averaged over about 10 individual measurements) are presented in Figs. 15(e) and (f). In total, for every sample, the relative grain boundary energies of 10 individual GBs were determined, and the resulting average values are listed in Table 6.

With increasing Bi contents up to 0.09 at.%Bi, i.e. within Region I, the relative GB energy, $\gamma_{gb}/\gamma_{s}$, increases slightly. In Region II for Bi contents from 0.09 to 0.23 at.%, an abrupt enhancement of $\gamma_{gb}/\gamma_{s}$ by more than 50% of the magnitude is seen. In general, the grain boundary energy is expected to decrease with the increase in Bi content in the Ni-Bi alloys. However, the direct experimental investigations suggest that the surface segregation is stronger than the grain boundary segregation,

Fig. 15. The back-scattered electron (BSE) image of pure Ni (a) and of the Ni-0.28 at.% Bi alloy (b) after annealing at 800 K for 24 h and the corresponding 3D AFM images of the GB grooves (c, d). The averaged line topography profiles acquired normal to the groove lines for Ni (e) and the Ni-0.28 at.% Bi alloy (f) are shown. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
see e.g. the brilliant measurements of Lopez et al. for the Cu-Bi alloys [69]. Thus, it is possible that the surface energy might decrease with the increase in Bi content in the Ni-Bi alloys. The measured GB energies support further the GB diffusion map presented in Fig. 13.

Having measured the surface energies of the Ni-Bi alloys independently, one would be able to plot the grain boundary diffusivity vs. grain boundary energy maps which may provide important insights on the influence of varying grain boundary energy on the grain boundary diffusivity with increasing Bi content.

4. Conclusions

Grain boundary segregation, grain boundary phases, their evolution and impact on GB kinetic properties of Ni-Bi alloys are investigated by a correlative approach using tracer diffusion and analytical microscopy methods. Tracer grain boundary diffusion was measured in the formal Harrison’s B- and C-type kinetic regimes applying the $^{65}$Ni radioisotope. Ni GB diffusion was measured for a set of well-characterized Ni-Bi alloys in the temperature range from 650 K to 1223 K. The major conclusions are as follows:

1) The results on Ni GB self-diffusion in pure Ni are in a good agreement with the literature values and the GB width is estimated as 0.64 nm.

2) The Ni tracer diffusion measurements in the Ni-Bi alloys reveal three characteristic regions of the dependence of the grain boundary diffusivity of Ni on Bi concentration. High-resolution TEM examination allowed to explain the diffusion data in terms of Bi alloying-induced GB phase transformations from Bi segregation (Region I) to continuous bilayer, tri-layer and multi-layer adsorption (Region II), and finally to the formation of an intergranular film (Region III). The results are fully supported by the measurements of relative grain boundary energies, $\gamma_b/\gamma_s$, using the thermal grooving method.

3) The correlative atomic structure-kinetic property measurements provide unique insights into the interplay of GB structure transitions and the resulting diffusion behaviour in polycrystalline materials. The formation of a liquid-like GB film with a drastically enhanced diffusivity indicates the importance of GB phase transitions for the properties of technologically important materials.

4) A grain boundary diffusion map for the Ni-Bi system is constructed. The GB diffusion map is correlated with the results of HRTEM investigations at 1123 K and the distinct changes of the GB diffusion rates at specific Bi concentrations are explained in terms of an evolution of the Bi coverage of general high-angle GBs.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.actamat.2022.118632.

References


Table 6
The averaged relative GB energies, $\gamma_b/\gamma_s$, of the Ni-Bi alloys.

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<td>$\gamma_b/\gamma_s$</td>
<td>0.42 ± 0.06</td>
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