Grain boundary width, energy and self-diffusion in nickel: Effect of material purity

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Abstract

The effect of material purity on grain boundary (GB) width and energy is investigated by GB self-diffusion measurements in Ni. The effect of matrix purity is examined for the first time for the low temperature C regime of GB diffusion. Grain boundary self-diffusion is measured in Ni of 99.99 wt.% purity in both B and C kinetic regimes, and the diffusional GB width \( d \) was determined as \( d = 0.6 \) nm. This result is in good agreement with previous measurements in 99.999 wt.% Ni. Thorough analysis of all available results on GB width in different coarse-grained and nanograin materials suggests that the diffusional GB width is independent of temperature, material purity and material nature and can be taken as \( 0.5 \) nm in undeformed materials. Grain boundary self-diffusion strongly depends on the amount of residual impurities, and the effect is marginal for less pure materials, \( D_{gb}^{99.99} : D_{gb}^{99.999} \approx D_{gb}^{99} : D_{gb}^{99.999} \approx D_{gb}^{99.6} : D_{gb}^{99.999} \) at low temperatures in Ni of the indicated purity levels. The effective dependence of the GB energy and the self-diffusion coefficient on grain size in a material of a given purity level is evaluated within the framework of a newly developed model.

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Keywords: Ni; Grain boundary diffusion; Grain boundary width; Grain boundary energy

1. Introduction

Many important properties of polycrystalline materials are strongly influenced by grain boundaries (GB). Solute atoms can segregate to these planar defects to minimize the Gibbs energy of the system, and thereby affect the bulk properties of the material. Therefore, detailed characterization of GB is crucial for the thorough understanding of the structure–property relationship in advanced materials. Whereas pure metals represent model systems for fundamental research, commercially pure materials are typically used in technological applications. Residual impurities, especially critical ones, drastically modify the kinetic properties of interfaces.

The effect of purity on GB self-diffusion was studied for Cu [1] and Ni [2,3]. The measurements were performed mainly in the B kinetic regime after Harrison’s [4] classification (the C-type measurements were carried out only at one temperature in less-pure material [3]), and the GB diffusivities, \( P = \delta \cdot D_{gb} \), were solely determined. Here, \( \delta \) and \( D_{gb} \) are the GB width and the GB diffusion coefficient, respectively. It was demonstrated that 1 ppm of S in 99.999 wt.% pure Cu already causes a dramatic decrease in the \( P \) values with respect to that in nominally 99.998 wt.% pure Cu [1]. GB self-diffusion was also studied in Ni of significantly different purity levels, namely in 99.5 and 99.9945 wt.% pure Ni [2] and 99.6 and 99.999 wt.% pure Ni [3]. The main conclusion obtained for Ni was the same as for Cu: the purer the matrix, the larger the double product \( P \) and the smaller the corresponding activation enthalpy [1–3].

Although the effect of purity on GB self-diffusion has been measured, other GB properties were not usually analyzed. While most GB properties are hardly accessible by direct methods, GB width and energy can be obtained...
through GB self-diffusion measurements. Therefore, the effect of residual impurities on these GB characteristics can be investigated as well [3]; see below (section 4.1 and 4.3).

These are the C-type measurements, which allow the GB diffusion coefficients \(D_{gb}\) to be determined directly and, in combination with the corresponding B-type experiments, the value of the GB width \(\delta\) to be addressed via

\[
\delta = \frac{P}{D_{gb}}
\]

GB energy can be found using Gupta’s representation [5] of Borisov’s equation [6] from the data on bulk and GB self-diffusion coefficients. The knowledge of the influence of material purity on GB width, energy and self-diffusion is required for the prediction of material stability and lifetime. Moreover, during recent decades, the nanocrystalline and ultrafine grained materials have been the focus of intensive research around the world. Numerous data on diffusion, mechanical and other properties of ultrafine grained and severely deformed materials.

The present work is devoted to the study of the influence of matrix purity on GB width, energy and self-diffusion in Ni. New GB diffusion measurements in Ni of nominal 99.99 wt.% purity are performed, which, in combination with previous data for Ni materials of 99.6 and 99.999 wt.% purity [3], will provide a deep insight into the effect of microalloying on the interface properties. The effect of matrix purity is for the first time examined for the low temperature C regime of GB diffusion. The fundamental difference in the influence of residual impurities on GB properties of coarse- and nanograin materials is demonstrated in the framework of a newly developed model for the effective dependence of the GB energy and the self-diffusion coefficient on grain size. These effects are shown to be marginal for coarse-grained materials, but gain importance with decreasing grain size, particularly for nanocrystalline materials.

2. Experimental details

2.1. Sample preparation

For the present study, nickel of 99.99 wt.% purity was used. The chemical composition is reported in Table 1 and compared with that of Ni of nominal 99.999 and 99.6 wt.% purity levels used in a previous study [3]. The chemical analysis was performed by Mikroanalytisches Labor Pascher in Remagen-Bandorf, Germany.

The rods 10 mm in diameter were cut by spark erosion into disks 1 mm thick. Subsequently, the samples were ground and polished to a mirror-like quality by standard metallographic procedures.

The specimens were subjected to a recrystallization annealing at 1300 K for 3 h in order to remove the preparation-induced stresses and to stabilize the grain structure for subsequent diffusion measurements. After such an annealing, the recrystallization processes were completed, and no further grain growth was observed. Afterwards, the samples were additionally annealed at the same temperature and at least for double the duration of the subsequent diffusion annealing in order to approach an equilibrium segregation of residual impurities and to reduce potential GB migration. In the case of intended C-type diffusion measurements (i.e., under conditions when bulk diffusion is frozen; see below), the samples were annealed at slightly higher temperatures for several days. Before the heat treatment, samples were wrapped in cleaned high-purity nickel foil and sealed in silica tubes under a purified argon atmosphere. The temperatures were measured and controlled throughout the annealing treatment with certified Ni–NiCr thermocouples with an accuracy of ±1 K.

2.2. Microstructure characterization

The microstructure was characterized by scanning electron microscopy with a FEI Nova NanoSEM 230 device using the electron backscatter diffraction (EBSD) method. The grain size was found to be ~20 μm in the as-cast state (Fig. 1a), and it grew to ~500 μm after the above-mentioned pre-diffusional heat treatment (Fig. 1b). For comparison, the average grain sizes in 99.6 and 99.999 wt.% pure Ni after similar pre-diffusional heat treatment were determined as ~300 μm and >400 μm, respectively [3].

2.3. Radiotracer diffusion measurements

The GB self-diffusion was measured using the \(^{63}\)Ni radiotracer isotope (half-life 100 years), which was available as 0.5 M hydrochloric solution. The original radiotracer solution was highly dissolved in bi-distilled water to approach the specific radioactivity of ~3 kBq μl\(^{-1}\). Seven microliters were dropped onto the sample surface and dried. Before the application of the tracer, the sample surface was slightly etched by a solution of CH\(_3\)COOH and HNO\(_3\) (69%) in distilled water (2:2:1).

Temperatures and times of the annealing treatments were chosen in order, first to satisfy the conditions of the chosen kinetic regime and, second in order to obtain a reliable Arrhenius diagram over a wide temperature range.

After diffusion annealing, the samples were reduced in diameter by grinding (by ~1 mm) in order to eliminate the effects of lateral and surface diffusion. The diffusion penetration profiles were determined by the serial sectioning technique, using a precision parallel grinder with abrasive Mylar foils of 3–30 μm particle size. The section
thickness was determined by weighing the sample between grinding steps, using a microbalance. The radioactivity was measured by a liquid scintillation analyzer (TRI-CARB 2910, Canberra Co.). The tracer concentration in a section is proportional to the ratio of the counting rate after background subtraction from the section mass. Further experimental details can be found in Ref. [3].

3. Results

The analysis of GB penetration profiles strongly depends on the type of kinetic regime in which the measurements are performed [7]. In the case of the C-type kinetic regime, typically at low temperatures, tracer atoms diffuse along GB and do not penetrate into the grain interiors. At higher temperatures, diffusion is significant not only along GB, but also in the grain interior, and such conditions correspond to the B-type kinetic regime.

For the case of self-diffusion, the value of the parameter \( \alpha \), which describes the tracer leakage from GB into the grain interior, is given by

\[
\alpha = \frac{\delta}{2\sqrt{D_0 t}}
\]

and determines the given kinetic regime in the case of self-diffusion. Here, \( t \) is the annealing time, and \( D_0 \) is the bulk diffusion coefficient. In recent computer simulations, the C-type regime was identified for values of \( \alpha > 5 \) [8]. In practice, \( \alpha > 1 \) may be considered sufficient, taking into account experimental uncertainties [9]. Note that, since the penetration lengths are smaller than the average grain size, the parallel slab model of Fisher [10] can be directly applied. The conditions for the B-type regime are fulfilled for \( \alpha < 0.1 \) [7].

In the present case of self-diffusion, the required GB diffusion regime can be realized just by an appropriate choice of the annealing time \( t \), at the given temperature \( T \) (i.e., for the given value of the bulk diffusion coefficient \( D_v \)). In the case of polycrystalline materials, one has to be aware that, in the B-type regime, the bulk diffusion depth \( \sqrt{D_v t} \) must be smaller than the grain size in order to avoid interference with A-type kinetics [7].

The required bulk self-diffusion coefficient of Ni for further data calculation was taken from the work of Maier et al. [11]

\[
D_v = 9.2 \times 10^{-5} \exp \left( -\frac{278 \text{ kJ/mol}}{RT} \right) \text{m}^2 \text{s}^{-1}
\]

Here, \( R \) denotes the gas constant.

3.1. C-type diffusion measurements

The radiotracer experiments in the C-type regime were carried out at three different temperatures <700 K. This choice was inspired by the previous study of GB self-diffusion in Ni of 99.999 wt.% purity [3]. The measured concentration profiles are presented in Fig. 2a as a function of the penetration depth squared.

![EBSD maps of 99.99 wt.% pure nickel (a) in the as-cast state and (b) after a pre-diffusional annealing treatment.](image-url)
Here, $c$ is the layer tracer concentration in a section, and $y$ is the penetration depth. These coefficients as well as the relevant parameters of the diffusion experiments are given in Table 2.

3.2. B-type diffusion measurements

In the case of the B-type regime, concentration profiles are linearized in the coordinates of $\ln c$ vs. $y^{6/5}$, according to Le Claire’s analysis [12] of Suzuoka’s exact solution [13]. As a result, the double product $P = \delta \cdot D_{gb}$ can be obtained from the corresponding slope. The exact expression depends on the parameter $b$, which has to be $>10$ in the case of the B-type regime [7]

$$\beta = \frac{P}{2D_c \sqrt{D_t}}$$

(5)

The value of $\beta$ indicates the relative significance of fast GB diffusion in comparison with bulk diffusion.

In the most general case, when $\beta$ is $>10^4$, the double product is determined as:

$$P = 1.308 \sqrt{\frac{D_t}{t}} \left( -\frac{\partial \ln c}{\partial y^{6/5}} \right)^{-5/3}$$

(6)

At values $10^2 < \beta < 10^4$, Eq. (6) must be slightly modified as follows [7]

$$P = 2 \sqrt{\frac{D_t}{t}} \left( -\frac{\partial \ln c}{\partial y^{6/5}} \right)^{-5/3} \cdot (0.74 \beta^{0.005})^{5/3}$$

(7)

The experimental penetration profiles plotted against $y^{6/5}$ are presented in Fig. 2b.

The double products $P$ of GB diffusion were calculated using Eqs. (6) and (7) (see Table 2). A linear temperature

Table 2

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$t$ (h)</th>
<th>$\sqrt{D_t}$ (m)</th>
<th>$D_{gb}$ (m$^2$ s$^{-1}$)</th>
<th>$P$ (m$^3$ s$^{-1}$)</th>
<th>$a$</th>
<th>$\beta$</th>
<th>Kinetic regime</th>
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<td>584</td>
<td>1160</td>
<td>$7.1 \times 10^{-12}$</td>
<td>$1.3 \times 10^{-18}$</td>
<td>–</td>
<td>35</td>
<td>$3.7 \times 10^{12}$</td>
<td>C</td>
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<tr>
<td>620</td>
<td>329</td>
<td>$2.0 \times 10^{-11}$</td>
<td>$1.1 \times 10^{-17}$</td>
<td>–</td>
<td>12.5</td>
<td>$4.1 \times 10^{11}$</td>
<td>C</td>
</tr>
<tr>
<td>640</td>
<td>474</td>
<td>$5.6 \times 10^{-11}$</td>
<td>$6.4 \times 10^{-18}$</td>
<td>–</td>
<td>4.5</td>
<td>$1.6 \times 10^{10}$</td>
<td>C</td>
</tr>
<tr>
<td>762</td>
<td>456</td>
<td>$3.1 \times 10^{-9}$</td>
<td>–</td>
<td>$1.0 \times 10^{-24}$</td>
<td>$6.9 \times 10^{-2}$</td>
<td>$1.8 \times 10^{7}$</td>
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<tr>
<td>780</td>
<td>231</td>
<td>$4.2 \times 10^{-9}$</td>
<td>–</td>
<td>$2.0 \times 10^{-24}$</td>
<td>$5.9 \times 10^{-2}$</td>
<td>$1.1 \times 10^{7}$</td>
<td>B</td>
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<tr>
<td>950</td>
<td>17</td>
<td>$5.4 \times 10^{-9}$</td>
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<td>$2.3 \times 10^{-22}$</td>
<td>$4.7 \times 10^{-3}$</td>
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<td>–</td>
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<td>$1.5 \times 10^{-4}$</td>
<td>32</td>
<td>B</td>
</tr>
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</table>

Fig. 2. The experimental penetration profiles in (a) the C-type kinetic regime and (b) the B-type kinetic regime, $y$ is the penetration depth, $k$ is a scaling factor assigned individually to each profile to allow the different profiles to be distinguished.
dependence of the double product was observed for the temperature interval under consideration (Fig. 3), which results in the following Arrhenius relation:

$$P = 2.4^{\pm 0.7} \times 10^{-13} \exp \left( -\frac{(165 \pm 2) \text{kJ/mol}}{RT} \right) \text{m}^3 \text{s}^{-1} \quad (8)$$

4. Discussion
4.1. Grain boundary diffusional width

Combining the present measurements performed in both B- and C-kinetic regimes, the diffusional GB width $\delta$ can be determined (Eq. (1)). The GB width is found to be equal to 0.6 \(^{0.0}_{0.5}\) nm. This value is in good agreement (taking into account the experimental uncertainties) with previous measurements on 99.999 wt.% pure Ni (0.54 \(\pm\) 0.1 nm) [3] and with the commonly accepted value of 0.5 nm [14]. For comparison, the compilation of published data on the GB width as a function of the homologous temperature $T/T_m$ is given in Fig. 4 (here, $T_m$ is the corresponding melting point). It could be seen that all data obtained by diffusion measurements on pure metals ($\alpha$-Ti [15], Ag [16,17], Ni [3, this work]) as well as on compounds ($\gamma$-Fe–Ni [18], NiO [19]) are close to 0.5 nm. This value was also used to fit the diffusion data obtained in B- and C-kinetic regimes in $\alpha$-Fe [20] and $\gamma$-Fe–Ni [21] and seems to be a good approximation.

Results obtained by Fultz et al. [22] in nanocrystalline materials, using a completely different method (comparing plots of GB fractions vs. grain size to similar plots obtained from microstructures generated by Monte Carlo simulation following Johnson–Mehl–Avrami–Kolmogorov kinetics), showed values of $\delta$ that are slightly >1 nm in body-centered cubic and \(~0.6\) nm in face-centered cubic (fcc) Fe-based alloys. These results agree well with the GB width determined by high resolution transmission electron microscopy (HRTEM) observations in nanoscaled Pd, which vary from 0.2 to 1.1 nm [23–25]. The study by Champion and Hýtch [26] of nanoscaled Cu yielded a value of 0.3 nm. A study by Epperson [27] on nanoplate TiO$_2$ gave a value of \(~0.5\) nm. Moreover, the data recently obtained by Rösnér et al. [28] gave the interphase boundary (Pb/Al) width equal to 0.7 nm for high-angle boundaries.

The results obtained mainly on pure fcc metals and several oxides clearly demonstrate that the GB width $\delta$ does not depend on the material purity. Moreover, no such dependence on the grain size can be deduced (comparing, for example, Refs. [17] and [22–25]).

Although all experimentally determined values are close to 0.5 nm, the term “GB width” must be determined more specifically. From the above-mentioned data, two types of widths could be substantiated: the “diffusional GB width”, defined as the effective width of the zone of an enhanced diffusion rate along the GB; and the “structural GB width”, defined as the thickness of the region of a decreased planar long-range order. Segregation of impurities in a material could result in chemical effects on the GB diffusivity (as shown, for example, in the work of Bernardini et al. [29]). The recent investigation of Ni diffusion in nanocrystalline Cu of Chellali et al. [30] mentioned a third, the so-called “segregational” GB width, which represents the thickness of a segregation zone that could reach values up to 3 nm in width. Moreover, the authors of that study found a strong exponential temperature dependence of this parameter. However, any hypothetical temperature dependence of the “diffusional” GB width should lead to a curvature in the Arrhenius diagram at high temperatures (a positive deviation). Yet, neither 99.99 wt.% pure Ni (Fig. 3), nor 99.999 wt.% pure Ni [3] demonstrates any deviations of GB self-diffusion from a straight line in the entire temperature interval that has been investigated. Thus, the absence of any dependence on temperature of the “diffusional” GB width under these conditions can be concluded. Moreover, the direct comparison of GB widths obtained for nickel of different purities and for a large number of other metallic materials at different homologous temperatures does not exhibit any temperature dependence within the experimental uncertainties (see Fig. 4).

Further investigations on the hypothetical temperature dependence of the GB width would be of great interest. The temperature dependence of the “structural GB width” has not been reported experimentally so far. Based on molecular dynamics simulations, Keblinski and Yamakov [31] reported the temperature dependence of the GB diffusional width in Pd at high temperatures near the melting point. The total change in the GB width was within a factor
of 2. Note that such high temperatures are typically not accessible for GB diffusion experiments, owing to a concurrent strong contribution of bulk diffusion. Fig. 4 also substantiates that the GB widths obtained for all measured materials correlate with each other and with the commonly accepted value of 0.5 nm. This fact suggests that, within the experimental uncertainties, the GB thickness is independent of the material purity and nature. Notice the good correlation between the values of GB widths obtained by HRTEM studies (the structural GB width) and GB diffusion measurements (the diffusional width).

4.2. Effect of purity on GB self-diffusion

In Fig. 3, the present results are compared with previous data for nickel of 99.6 and 99.999 wt.% purities [3] obtained by the same technique and using the same equipment. The data obtained by Rothova et al. [2] are also shown for comparison. As a general trend, it is seen that the higher the purity of a material, the higher the GB diffusivity $P = \delta D_{gb}$, and the lower the effective activation energy for GB diffusion. It should be mentioned that different "critical" impurities, which strongly segregate at GB and which could dramatically affect the GB diffusion, might be present in different materials. It was shown that different reasons for GB retardation in the presence of impurities can exist: GB segregation [4,32–34] or chemical interaction of impurities in GB with the formation of atomic complexes [35]. Unfortunately, it is not possible to identify exactly the impurities responsible for this effect, because data on the impurity concentration in 99.5 and 99.9945 wt.% pure Ni [2] are not available at sufficient accuracy.

Fig. 3 suggests a strongly non-monotonous dependence of $D_{gb}$ on the purity of Ni, $D_{gb}^{99.999} \gg D_{gb}^{99.99} \approx D_{gb}^{99.6}$, especially at low temperatures. This result is similar to the results of Bernardini et al. [29] on Fe GB diffusion in Fe–Sn alloys, where the GB diffusivity, after a sharp initial drop, rapidly approached a “plateau” value with increasing Sn concentration in the alloy. However, analyzing these results, one has to keep in mind that coarse-grained polycrystalline materials are investigated with the grain size in the range 300–500 μm. The volume fraction of the “GB material” is $\sim 10^{-5}$ in this case, and $\sim 10$ ppm of a solute might be enough to cover all GB by a monolayer, thus drastically influencing the GB diffusion. In the case of ultrafine grained or nanocrystalline materials, this amount of a solute would not be sufficient to decorate the large area of the GB, and GB diffusion can proceed effectively as in a pure material. The effect of grain refinement on the effective purity of the material was discussed in a number of studies (see e.g., Refs. [36–39].

Combining the ideas of Kirchheim [37], Trelewicz and Schuh [38] and Weissmüller [39], which adopt the Gibbs adsorption theorem to the nanocrystalline alloys in order to include the grain size dependence of the GB energy, the dependence of the GB diffusion coefficient of the solvent atoms on grain size is now addressed. Using the Gibbs adsorption theorem [40] for a two-component ideal solution and isothermal conditions with Langmuir–McLean’s equation for GB segregation [41,42], one finds the dependence of GB energy on the composition of the bulk solution that was reported in a slightly different notation by Liu and Kirchheim [43]

$$\gamma - \gamma_0 = -RT \Gamma_0 \frac{s}{s - 1} \ln(1 + (s - 1)X_s)$$

where $\gamma$ and $\gamma_0$ are GB energies of a solid solution and a pure solvent, respectively, $X_s$ is a solute molar fraction in the bulk, $\Gamma_0$ is a solute monolayer excess, and $s = \exp(-\Delta G_s/RT)$ is a solute segregation coefficient ($\Delta G_s$ is the Gibbs segregation energy, and $\Delta G_s < 0$ in the case of segregation).
The GB energy $\gamma$ can be evaluated using Gupta’s representation [5] of Borisov’s equation [6] if the measurements of coefficients of GB and bulk self-diffusion are realized

$$\gamma = \frac{\lambda}{2} RT \ln \frac{D_{gb}}{D_v}$$

where $\lambda = \frac{1}{\Delta m N_A}$ with $\Delta m$ and $N_A$ being the mean distance between matrix atoms at the GB and Avogadro’s number, respectively.

The main problem here is the use of Borisov’s equation for the self-diffusion in alloys, since no one has analyzed the solute concentration limit at which Borisov’s equation can no longer be applied. Indeed, Guiraldenq [44] has derived Borisov’s equation in a slightly different way from that used in the original work, which allowed the original Borisov’s model to be applied even for the case of heterodiffusion in alloys. The comparison of GB energies calculated using Borisov’s equation with those measured independently by other techniques demonstrated that Borisov’s approach works perfectly in the case of heterodiffusion of tracers with properties similar to matrix atoms; nevertheless, in the case of a strongly segregating solute, the agreement between energies derived from solute and solvent diffusion data was not so convincing, although the deviations were not really large [44].

Gupta re-analyzed Borisov’s equation and derived it in a different way [45]. In that work, the GB energies derived via Borisov’s equation and those measured by creep experiments were compared for pure metals, Pb, Ag, Au, Cu and Ni, and excellent agreement was observed [45]. Consequently, Borisov’s approach seems to work well at least for the five above-mentioned pure metals (purity levels were not precise), including Ni, which is the object of this paper. Note that the model of grain size influence on GB self-diffusion in alloys that is being developed can be applied only to the systems and to the concentration range of a solute where Borisov’s equation gives reliable data, which is assumed for the present study of Ni of high purity levels (99.6, 99.99 and 99.999%). The present authors’ re-casting of Borisov’s original approach to the case of binary system with a strongly segregating impurity is added as an Appendix. The GB diffusion coefficient of solely solvent atoms is considered as a probe of the impurity-induced change of GB energy, and the subsequent consideration is not applicable for diffusion of solute atoms.

Introducing Borisov’s Eq. (10) in Eq. (9) and after regrouping, one obtains

$$\frac{D_{gb}}{D_{gb}^{pure}} = \frac{D_v}{D_v^{pure}} (1 + (s - 1)X_s) \frac{\gamma_{gb}}{\gamma_{gb}^{pure}}$$

(11)

where $D_{gb}^{pure}$ and $D_v^{pure}$ are GB and bulk self-diffusion coefficients in a pure solvent.

For strongly segregating species ($s \gg 1$), using the condition that $\Gamma_0/\lambda \approx 1$ and considering the linear dependence of bulk self-diffusion on the solute content [46], one can rewrite Eq. (11) as

$$D_{gb} \approx D_{gb}^{pure} (1 + bX_s)(1 + sX_s)^{-2}$$

(12)

Here, $b$ is the solute enhancement factor, $D_v = D_v^{pure}(1 + bX_s)$. Note that in the case of a small amount of the solute atoms, i.e., $bX_s \ll 1$ and $sX_s \ll 1$, Eq. (12) reduces to $D_{gb} \approx D_{gb}^{pure}(1 + (b - 2s)X_s)$, which was proposed by Bernardini et al. [29] in slightly different notation for the corresponding changes in the double products $P = \delta \cdot D_{gb}$ and $P^{pure} = \delta^{pure} \cdot D_{gb}^{pure}$. This expression was experimentally verified for iron–tin alloys by Bernardini et al. [29] for GB diffusivities $P$, since only B-type measurements were accessible in those studies.

In the next step, the grain size dependence is introduced. According to Kirchheim [47], a solute molar fraction in the

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1 It can be shown that $\Gamma_0/\lambda \approx \frac{1}{\Delta s}$, with $\Delta s$ being the mean distance between solute atoms along the interface in the case of monolayer coverage. For estimates, the approximation $\lambda/\lambda_s \approx 1$ is used.
bulk depends on the grain size $d$. For spherical grains, one has

$$X_v = X_{tot} - \frac{a}{V} \Omega_M \Gamma = X_{tot} - \frac{3 \Omega_M}{d} \Gamma$$

where $X_{tot}$ is the total molar fraction of a solute in the system, $\Omega_M$ is the molar volume of matrix atoms, $a$ is the total GB area, $V$ is the volume of the system, and $\Gamma$ is the GB solute excess.

Using Langmuir–McLean’s isotherm, Eq. (13) can be re-written as

$$X_v = X_{tot} - \frac{3 \Omega_M}{d} \left( \frac{\Gamma_0 X_c}{1 + (s - 1) X_v} \right)$$

Introducing the critical grain size $d_c$, $d_c = 3 \Omega_M \Gamma_0 s$, and solving the equation for $X_v$, when $s \gg 1$, one obtains

$$X_v = \frac{- (1 + \frac{d_c}{d} - s X_{tot}) + \sqrt{(1 + \frac{d_c}{d} - s X_{tot})^2 + 4 s X_{tot}}}{2s}$$

This expression, together with Eq. (12), represents the obtained dependence of the GB diffusion coefficient of solute atoms on grain size. At $d < d_c$, the grain size strongly affects GB self-diffusion in an impure matrix with $D_{gb} \rightarrow D_{gb}^{pure}$ at $d \rightarrow 0$. Otherwise, $X_v \approx X_{tot}$, and the influence of grain size on GB self-diffusion is negligible.

The parameters entering Eq. (15) for self-diffusion in Ni are now estimated by an order of magnitude. The present authors’ analysis, according to Gupta’s approach [5] (according to the scheme described comprehensively in Ref. [3]), yielded the segregation enthalpy of a “critical” impurity of $\sim 38 \text{ kJ mol}^{-1}$ in Ni of 99.99 wt.% purity. Thus, the segregation factor $s$ at 500 K is $\sim 10^4$. $\Gamma_0$ can be estimated as $\sim 2.5 \times 10^{-5} \text{ mol m}^{-2}$; the molar volume of Ni is $6.6 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ at room temperature. These estimates give us the critical grain size of $2 \mu m$ at 500 K.

Assuming that the data on GB self-diffusion in Ni of 99.999 wt.% purity [3] correspond to the self-diffusion in pure Ni and neglecting the dependence of bulk diffusion on material purity (this can be done since $bX_v \ll 1$ for fcc metals when $X_c \ll 10^{-3}$, see e.g., Refs. [46,48,49]), the Ni GB self-diffusion coefficient is plotted as a function of purity and the grain size $d$ (Fig. 5).

For coarse-grained Ni ($d \gg 2 \mu m$), GB self-diffusion is independent of the grain size and depends strongly on the impurity content. A decrease in the grain size to $d \ll 2 \mu m$ leads to a strong increase in the GB self-diffusion coefficient, and it approaches the value of GB self-diffusion in pure Ni. The influence of grain size is more pronounced if the total amount of impurities is increased. Fig. 5 suggests that grain refinement results in effective “purification” of the material with respect to its interface properties.

To analyze the experimental results in the framework of the proposed model, the nature and amount of a “critical” impurity should be known. The basic hypothesis of the present study was that Si is the critical impurity in all three Ni materials studied (99.6, 99.99 and 99.999 wt.% purity). However, the present authors’ analysis according to Gupta’s approach [5] yielded the segregation enthalpy of a “critical” impurity of $\sim 38 \text{ kJ mol}^{-1}$ for 99.99 wt.% Ni, which differs remarkably from the value of $\sim 23 \text{ kJ mol}^{-1}$ derived for 99.6 wt.% Ni [3]. This result strongly suggests the presence of different “responsible” or “critical” impurities in the two Ni materials. It is probably Si in 99.6 wt.% Ni and S in 99.99 wt.% Ni. Thus, in the present case, one can obtain only qualitative (semi-quantitative) results using this model. The full quantitative analysis could be done on Ni micro-alloyed by different amounts of the same impurity, which is now pursued.

### 4.3. Grain boundary energy

According to Gupta’s representation [5] of Borisov et al.’s semi-empirical relationship [6], the following temperature dependence of the GB energy for the present Ni material of 99.99 wt.% purity is derived:

$$\gamma_{gb} = (9 \pm 3) \times 10^{-5} T + (0.77 \pm 0.02) \text{ J m}^{-2}$$

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$\gamma_{gb}$ (J m$^{-2}$)</th>
<th>Reference</th>
<th>Technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>330</td>
<td>5.3*</td>
<td>Kirchheim et al. [50]</td>
<td>Measurements of the electrochemical potential</td>
</tr>
<tr>
<td>–</td>
<td>1.1*</td>
<td>Klement et al. [51]</td>
<td>Differential scanning calorimetric measurement</td>
</tr>
<tr>
<td>300 K</td>
<td>1.4–1.6*</td>
<td>Van Swygenhoven et al. [52]</td>
<td>Molecular dynamics simulation</td>
</tr>
<tr>
<td>–</td>
<td>1.1–1.4*</td>
<td>Olmsted et al. [53]</td>
<td>Free surface energy and groove angle measurements (zero creep technique)</td>
</tr>
<tr>
<td>900–1400 K</td>
<td>1.3–1.6*</td>
<td>Mendelev et al. [54]</td>
<td>Diffusion measurements</td>
</tr>
<tr>
<td>–</td>
<td>0.84</td>
<td>Murr et al. [55]</td>
<td></td>
</tr>
<tr>
<td>1333</td>
<td>0.87</td>
<td>Murr [56]</td>
<td></td>
</tr>
<tr>
<td>1523</td>
<td>0.74</td>
<td>Hayward and Greenough [57]</td>
<td></td>
</tr>
<tr>
<td>1573</td>
<td>0.47</td>
<td>Clark et al. [58]</td>
<td></td>
</tr>
<tr>
<td>1643</td>
<td>0.93</td>
<td>Roth et al. [59]</td>
<td></td>
</tr>
<tr>
<td>1726</td>
<td>0.69</td>
<td>Hayward and Greenough [57]</td>
<td></td>
</tr>
<tr>
<td>1728</td>
<td>0.83</td>
<td>Divinski et al. [3]</td>
<td></td>
</tr>
<tr>
<td>1728</td>
<td>0.93 ± 0.04</td>
<td>Present work</td>
<td></td>
</tr>
</tbody>
</table>

* Values were obtained on nanocrystalline samples.
The GB energy is plotted in Fig. 6 as a function of temperature. $\gamma_{gb}$ increases with temperature in less pure materials, while it decreases in the purest 99.999 wt.\% Ni. At the melting temperature, $\gamma_{gb}$ approaches a common value of $(0.87 \pm 0.06) \text{J m}^{-2}$, since the impurity segregation decreases with increasing temperature. Moreover, it is clearly seen that impurities decrease the GB energy, which may be important for the stabilization of the grain structure in nanocrystalline materials [37].

In Table 3, the available experimental data on GB energies in Ni obtained by different methods are compared with the present data extrapolated to the melting temperature. A good agreement between the data on coarse-grained nickel can be seen, while the GB energies obtained on nanocrystalline samples are the largest. The atomistic simulation predicts GB energies that overestimate systematically the experimentally determined values.

5. Conclusions

Grain boundary width and energy were investigated by radiotracer self-diffusion measurements in polycrystalline Ni as a function of its purity. The following results can be highlighted.

1. Impurities have a strong effect on GB diffusion, and the purer the matrix, the faster the GB diffusion and the lower the corresponding activation enthalpy. The effect is the most pronounced for small additions of a solute, and a saturation effect on GB self-diffusion is observed.

2. The GB width is measured to be similar in all Ni materials of different purity levels as well as for other materials under consideration and, within experimental uncertainties, represents a temperature-independent value.

3. A model that predicts the dependence of GB diffusion coefficient of solvent atoms on material purity and grain size is proposed. The quantitative comparison with the model requires the knowledge of the quantity and type of “critical” impurities. It is shown that a decrease in the grain size can yield an effective enhancement of GB self-diffusion in less pure matrixes towards the values typical for a pure material. The effect is most pronounced for the nanoscaled materials.

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Appendix A

Here, the present authors give further insights into the basic formalism and present some ideas on why the GB diffusion rate of the solvent atoms, on the one hand, and the GB energy, on the other, vary in a correlated manner with addition of a strongly segregating impurity.

Consider the following two cases: a pure metal A and a binary system A–B (B is a strongly segregating element, and the volume fraction of B in the alloy is small). Borisov’s original approach (see Fig. A1) corresponds to the following main assumptions (the consideration is limited to vacancy-mediated diffusion only):

- $U_e^* \approx U_{gb}^* + e$.
- $U_e \approx U_{gb}$.
- A thermodynamic equilibrium exists between the bulk and the GB, which implies the same jump frequencies across and along the GB for matrix atoms (this point was never explicitly stated by Borisov’s and co-workers, but follows directly from Eq. (1) in Ref. [6]).

These assumptions are of empirical nature, but it was proved that they provide reasonable data for pure metals; see above (section 4.2). Now, consider the case of a strongly segregating impurity and analyze the diffusion of the solvent atoms only (considering the vacancy-mediated mechanism). Following Borisov et al., the modified energy levels are shown in Fig. A1 (dashed lines). There are generally two effects:

1. The GB energy is decreased from $e$ to $e'$, $\Delta e = e - e'$, as a result of solute segregation. This decrease can be described rigorously within the Gibbs adsorption theorem.

2. Following the reasoning of Surholt and Herzig [1] and Mishin and co-workers [60], one may prescribe all changes in the activation energy of solvent atoms due to segregation of solute atoms to the corresponding change of the vacancy migration energy (see Fig. A1):

$$\Delta Q_m = (U_{gb}^* - U_{gb}) - (U_{gb}^* - U_{gb}')$$  \hspace{1cm} (A1)
Now, it is assumed that $\Delta e \approx \Delta Q_{m}$, i.e., that the change in the solvent migration energy of GB diffusion follows the corresponding change in GB energy.

This assumption corresponds to the following model. The solute atoms segregate at some favorite places at the boundary and do not take part in the subsequent diffusion process. The “embryos” of two-dimensional phases are formed, and part of the solvent atoms is also immobilized. The GB area with these embryos may be considered as bulk-like, and the corresponding atoms must not be counted when one performs averaging for the migration energy change and the GB energy change. Thus, one must count all mobile GB atoms for the corresponding averaging procedures, and the applicability of Borisov’s approach for these atoms is assumed. Since these are, by definition, only solvent atoms (the solute atoms are immobilized), the respective changes in GB diffusivity and GB energy are correlated.

References