



Predicting grain boundary energies of complex alloys from ab initio calculations

Changle Li^a, Song Lu^{a,*}, Levente Vitos^{a,b,c}

^a Applied Materials Physics, Department of Materials Science and Engineering, KTH Royal Institute of Technology, Stockholm SE-10044, Sweden

^b Department of Physics and Astronomy, Division of Materials Theory, Uppsala University, Box 516, Uppsala SE-75120, Sweden

^c Research Institute for Solid State Physics and Optics, Wigner Research Center for Physics, P.O. Box 49, Budapest H-1525, Hungary

ARTICLE INFO

Article history:

Received 30 December 2020

Revised 15 June 2021

Accepted 29 June 2021

Available online 10 July 2021

Keywords:

Grain boundary energy

Surface energy

Ab initio

Fcc metals

ABSTRACT

Investigating the grain boundary energies of pure fcc metals and their surface energies obtained from *ab initio* modeling, we introduce a robust method to estimate the grain boundary energies for complex multicomponent alloys. The input parameter is the surface energy of the alloy, which can easily be accessed by modern *ab initio* calculations based on density functional theory. The method is demonstrated in the case of paramagnetic Fe-Cr-Ni alloys for which experimental grain boundary data is available.

© 2021 The Authors. Published by Elsevier Ltd on behalf of Acta Materialia Inc.

This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>)

Grain boundary (GB) plays a critical role in the microstructural evolution of polycrystalline materials [1,2]. The structures and energetics of GBs are closely related to various physical and mechanical properties, e.g., alloying segregation, precipitation, coarsening, or crack. Particularly, tailoring the properties of GBs by, e.g., controlling the element segregation/depletion, has been an important strategy for improving mechanical properties of alloys, and it is often referred to as the 'grain boundary engineering' [3,4]. The GB geometry is described by the five degrees of freedom (DOFs). For a complete description, two degrees are assigned to the rotation axis, one for the misorientation angle, and the other two for describing the normal of the GB plane [5]. As a key feature, the GB energy (GBE, or γ_{GB}) varies significantly with both misorientation and inclination [6,7], which makes accurate determination of the GBEs a great challenge in both experimental measurements and computational simulations.

Experimentally, the GBEs for randomly high-angle GBs are usually estimated from the geometries of the surface triple junctions or internal GB triple junctions in zero-creep experiments [8]. Often, it is the relative GBE or the GBE anisotropy that are determined [9,10]. For example, measuring the groove angle at the equilibrium junction composed of grain boundary and surface, the GBE to surface energy ratio can be determined [11–13]. Assuming that the surface energy is known, the GBE can be determined. Similar procedure has been applied for the evaluation of the low- and

high-angle GBEs, as well as the twin boundary energies [14–17]. Unfortunately, the surface energy itself is a quantity difficult to determine accurately by experiments, especially at low temperatures. Most of the available room temperature experimental surface energy were obtained indirectly by extrapolating the surface tension measured in the liquid phase [18–20]. The GBE can also be determined indirectly using diffusion data. Borisov [21] proposed a semi-empirical relationship between the increase of the self-diffusion in the GB relative to the bulk and the absolute GBE. This method was examined by Pelleg [22] and a satisfactory agreement between directly measured GBEs and the calculated ones was reported for a few close-packed cubic metals. The same method has been applied to alloys (e.g., Au-Ta alloys [23,24] and Ni alloys [25]). Overall, despite the existing experimental methods for GBE determination, it is cumbersome to perform these measurements considering the large number of GB types and their composition, temperature, and magnetic state dependences.

Alternatively, GBs can be investigated by atomistic simulations using empirical potentials or density functional theory (DFT) calculations. Potentials using embedded atomic method (EAM) applied for the GB studies in pure metals [26–31] led to improved understanding of the atomic structures and their energetics. For example, Holm et al. [32,33] calculated the GBEs for a large number of GBs in pure face-centered cubic (fcc) metals and found that the GBEs in different materials are strongly correlated. Olmsted et al. [33] showed that the GBEs are more influenced by the grain boundary plane than the misorientation angle. Studies based on DFT are usually more accurate and have a better predictive

* Corresponding author.

E-mail address: songlu@kth.se (S. Lu).

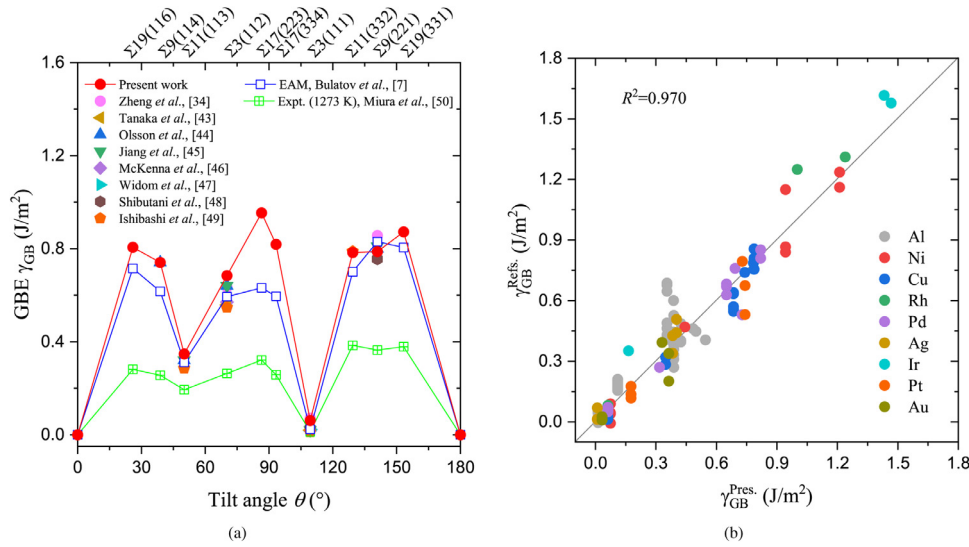


Fig. 1. (Color online) Theoretical and experimental GBEs for ten selected fcc metals. (a) Comparison between the present and previous γ_{GB} values for Cu as a function of the $[110]$ tilt angle θ . The previous DFT (solid symbols) [34,43–49], EAM (squares) [7] and the high temperature experimental (squares with plus, in arbitrary unit) [50] data are indicated. On the top of the figure, we show the ten GBs for which the present *ab initio* calculations were performed. (b) Comparison between the present ($\gamma_{GB}^{Pres.}$) and previous ($\gamma_{GB}^{Ref.}$) [34,43–49,51–66] DFT results obtained for the ten selected metals (shown in the legend) and ten tilt angles (not shown). Numerical values are listed in Table S2 in SM. The R^2 value obtained for the linear fit considering all selected metals shows a high degree of correlation. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

power as compared to methods based on empirical potentials. On the other hand, DFT calculations are often limited to pure metals or simple alloys and to low-index coincidence site lattice (Σ) types of GBs due to the extensive computational burden [34–36].

In the present work, we adopt DFT calculations to study the correlation between the GBEs of various fcc metals and between the GBEs and the surface energies. We show that the GBEs of the same macroscopic GB structures in a pair of fcc metals are strongly correlated via a material dependent factor (δ). This parameter can be estimated from the ratio of the low-index surface energies. Considering that DFT methods for studying the surfaces of pure metals [37,38] and alloys [39] have readily been established, the present development puts forward a feasible method for predicting the GBEs of complex alloys using their surface energies.

Ten types of the $[110]$ tilt GBs in ten fcc metals ($X = \text{Al, Cu, Au, Ag, Ni, Pd, Pt, Co, Rh, and Ir}$) were calculated by the Vienna *ab initio* Simulation Package (VASP) [40] using the projector augmented wave (PAW) method [41]. The atomic structures of these GBs are presented in Table S1 and Fig. S1 in the Supplementary Material (SM). For the exchange-correlation functional we adopted the generalized gradient approximation parameterized by the Perdew, Burke, and Ernzerhof (PBE) [42]. The k -point meshes were carefully tested to ensure the convergence of the GBEs within ~ 0.02 J/m². Cutoff energies were set to 500 eV for all metals. Full geometry relaxation was performed and the convergence criteria for electronic energy and force calculations were 10^{-5} eV and 0.02 eV/Å, respectively.

In Fig. 1(a), we show the calculated γ_{GB} for Cu as a function of the $[110]$ tilt angle θ , in comparison with the previous DFT values [34,43–49] as well as the EAM results [7]. The available experimental GBEs for different tilt angles at high temperature are also included. The DFT results agree well with each other, showing the typical shape of the γ -surface for the $[110]$ tilt GBs with two energy minima located at $\Sigma 3(111)$ (corresponding to $\theta = 109.47^\circ$) and $\Sigma 11(113)$ ($\theta = 50.48^\circ$) twin boundaries. The EAM and experimental γ -surfaces show the same shape [7,50] although the absolute values are somewhat smaller than the DFT results. The deviations between the DFT and experimental values can partly be described to thermal effects, which were neglected in the DFT cal-

culations. In addition, the experimental results are presented relative to the Cu/SiO₂ interfacial energy [50] and there is a large uncertainty in the measured temperature dependence [50]. Therefore, here we should focus on the qualitative comparison, i.e., the shapes of the γ -surfaces when contrasting to the experimental results. In fact, the γ -surfaces with similar cusps are observed for all the studied fcc metals. In Fig. 1(b), we compare the present GBEs for all fcc metals with the available DFT results [34,43–49,51–66] (numerical values are listed in Table S2 in SM). Overall, the present GBEs have an excellent agreement with the former DFT values, with $R^2 = 0.97$ and a standard error of ~ 0.017 J/m².

Starting from the present DFT results for the GBEs, we examine the correlation between the GBEs in different metals. Here, we choose Cu as the reference and compare the GBEs of the same GB structure in different materials. We notice however that choosing another metals as reference leads practically to the same conclusions. Results for four elements, Al, Ni, Pd, and Pt, taken as examples of *sp*, *3d*, *4d*, and *5d* metals, respectively, are shown in Fig. 2. In order to strengthen our point, some previous DFT results for tilt and twist GBs [34] are also included in the figure. We emphasize that the following observations and discussions apply to all metals considered here and the detailed results can be found in SM (Fig. S2 and Table S2). First, we confirm that there is a clear correlation between the GBEs in different metals, as demonstrated by the previous EAM results [67]. All the boundary energies in a specific metal locate approximately on a straight line passing through the origin (dashed line in Fig. 2), indicating that a single material dependent factor (δ) may be used to correlate the GBEs in a pair of metals, i.e., $\gamma_{GB}^A(\text{DOF}) \approx \delta \gamma_{GB}^{\text{Cu}}(\text{DOF})$ (A stands for an fcc metal). The slopes ($\delta_{GB(\text{fit})}^{A/\text{Cu}}$) of the linear fitting for all 9 metals are listed in Table 1. The mean-absolute error and root-mean-square error are usually less than 0.1 J/m² (Table 1). The nearly perfect scaling relation between the GBEs in different metals highlights the critical roles played by the GB structures in deciding the GBEs, which is consistent with previous EAM results [32] and experimental observations [6]. The anisotropy of GBEs is, to the first order approximation, decided by the boundary structure, i.e., the five macroscopic DOFs in crystalline structure. In other words, despite of the existence of the difference in local atomic structure configuration

Table 1

Surface energies for the (100) and (111) surface facets ($\gamma_{S(100)}$ and $\gamma_{S(111)}$, respectively) and their ratios relative to that of Cu for the selected fcc metals. $\delta_{GB(fit)}^{A/Cu}$ is the gradient of the linear fitting of the DFT GBEs in Fig. 2 and Fig. S2. $\gamma_{GB}(\delta_{S(100)}^{A/Cu})$ and $\gamma_{GB}(\delta_{S(111)}^{A/Cu})$ are the predicted GBEs using the (100) and (111) surface energies, respectively. $\gamma_{GB}^{expt.}$ are the experimental GBEs (references indicated). All the DFT calculations correspond to the static state (0 K), and the experimental GBEs for the general high-angle GBs are obtained by linear extrapolation to 0 K (the effect of nonlinear temperature dependence is negligible for the present purpose, see relevant discussion and Fig. S3 in SM). $\overline{\gamma_{GB}}$ is the equal-weight average over the obtained high-angle GBEs of [110] tilt GBs except $\Sigma 3(111)$ and $\Sigma 11(113)$ (see Notes in SM).

	DFT					Predicted			Expt.
	$\gamma_{S(100)}$ (J/m ²)	$\gamma_{S(111)}$ (J/m ²)	$\delta_{S(100)}^{A/Cu}$	$\delta_{S(111)}^{A/Cu}$	$\delta_{GB(fit)}^{A/Cu}$ (MAE ^j , RMSE ^k)	$\gamma_{GB}(\delta_{S(100)}^{A/Cu})$ (J/m ²)	$\gamma_{GB}(\delta_{S(111)}^{A/Cu})$ (J/m ²)	$\overline{\gamma_{GB}}$ (J/m ²)	$\gamma_{GB}^{expt.}$ (J/m ²)
Cu	1.44 ^a	1.30 ^a						0.81	0.78 ^c
Al	0.92 ^a	0.82 ^a	0.64	0.63	0.56 (0.048, 0.063)	0.50	0.49	0.46	0.44 ^d
Au	0.86 ^a	0.71 ^a	0.60	0.55	0.49 (0.027, 0.036)	0.46	0.42	0.39	0.40 ^e
Ag	0.84 ^a	0.76 ^a	0.59	0.58	0.57 (0.019, 0.022)	0.45	0.45	0.46	0.46 ^f
Ni	2.22 ^a	1.92 ^a	1.54	1.48	1.38 (0.052, 0.068)	1.20	1.15	1.12	1.11 ^g
Pd	1.51 ^a	1.33 ^a	1.05	1.02	0.96 (0.021, 0.027)	0.81	0.79	0.78	0.80 ^h
Pt	1.85 ^a	1.49 ^a	1.28	1.15	1.01 (0.069, 0.080)	1.00	0.89	0.81	0.84 ⁱ
Rh	2.35 ^a	2.01 ^a	1.63	1.55	1.71 (0.081, 0.107)	1.27	1.20	1.44	
Ir	2.84 ^a	2.06 ^a	1.97	1.58	2.12 (0.091, 0.118)	1.53	1.23	1.71	
Co	2.46 ^b	2.02 ^b	1.71	1.55	1.45 (0.096, 0.101)	1.33	1.21	1.17	

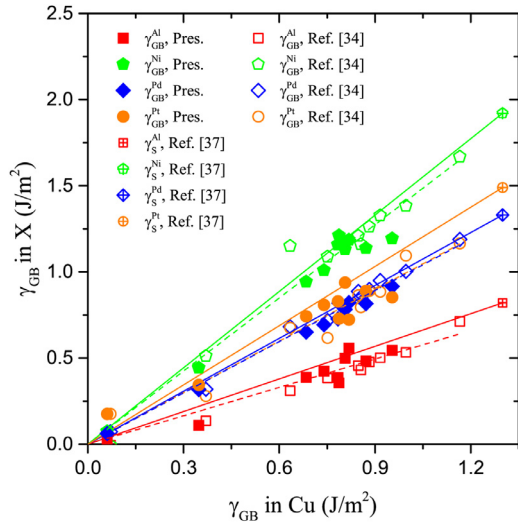
^a Ref. [37].^b Ref. [38].^c Ref. [24].^d Refs. [16,17,68].^e Ref. [24].^f Refs. [16,22,68].^g Refs. [14,69,70].^h Refs. [68,70–72].ⁱ Refs. [73,74].^j Mean absolute error (MAE) (J/m²).^k Root mean square error (RMSE) (J/m²).

Fig. 2. (Color online) Pairwise comparison of the calculated γ_{GB} (solid symbols) and the (111) surface energies (open symbols with plus) for Al, Ni, Pd, and Pt with Cu obtained at 0 K. The dashed lines are the linear fits to the GBEs. Previous DFT GBEs (open symbols) for tilt and twist GBs from Ref. [34] are included in the linear fitting. The DFT surface energies are taken from Ref. [37]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

(or even in magnetic environment), the GBEs in different materials may be described by an universal functional of the five geometric parameters in different materials. This observation follows closely the concept developed by Bulatov et al. [7].

In literature, the GBEs were usually proposed to scale with physical parameters like shear modulus ($a_0 c_{44}$) or Voight average shear modulus ($a_0 \mu$), cohesive energy (E_0/a_0^2), stacking fault energy (SFE, γ_{SF}) or their combinations [32,34,67]. The shear moduli and cohesive energy were rescaled by the lattice parameter (a_0) to

give the same units as the GBE. The rationale behind the relation between the GBE and shear modulus μ , e.g., $\gamma_{GB} \approx k a_0 \mu$ (k , a coefficient) is from the Read-Shockley type of dislocation model [75]. There, the GBs with low misorientation angles are considered to be composed of arrays of dislocations whose energies are proportional to the shear modulus [32]. Therefore, the material dependent scaling factor δ that connects the GBEs in two materials is thought to be related to the ratio of $a_0 c_{44}$ or $a_0 \mu$ (denoted as $\delta_{a_0 c_{44}}^{A/B}$ and $\delta_{a_0 \mu}^{A/B}$ in the following). Holm et al. [32] showed that the ratios of both $a_0 c_{44}$ and $a_0 \mu$ are very close to the actual slope of the linear fit of the EAM GBEs for metals with low SFEs; while for metals with high SFEs like Al, the ratio of $a_0 c_{44}$ acts as a better scaling factor than that of $a_0 \mu$. However, Ratanaphan et al. [67] reported that the ratio of the cohesive energies ($\delta_{E_0/a_0^2}^{A/B}$) is a much better

indicator than the ratios of $a_0 c_{44}$ or $a_0 \mu$ in bcc metals. It is argued that the GBEs scale with the cohesive energy based on the broken bond model of GBE [76]. But in fcc metals, previous EAM results [29,32] found that for a specific type of GB, the GBE does not follow a linear relationship with E_0/a_0^2 in different fcc metals. Furthermore, DFT calculations by Zheng et al. [34] confirmed that no general positive correlation between the GBE and the cohesive energy exists. As for the SFE, it is strongly related to the coherent twin boundary energy, $\gamma_{SF} \approx 2\gamma_{tw}$, but correlates weakly with the general GBEs [32]. Here we reconsider this question and analyze the correlations between the above parameters. In Fig. 3(a) and (b), we compare $\delta_{a_0 c_{44}}^{A/Cu}$, $\delta_{a_0 \mu}^{A/Cu}$, $\delta_{E_0/a_0^2}^{A/Cu}$, and $\delta_S^{A/Cu}$ with $\delta_{GB(fit)}^{A/Cu}$ from DFT/experiment and EAM calculations, respectively. All available data in the studied metals are listed in Tables in SM. $\delta_{a_0 c_{44}}^{A/Cu}$ shows better consistence with $\delta_{GB(fit)}^{A/Cu}$ than $\delta_{a_0 \mu}^{A/Cu}$ and $\delta_{E_0/a_0^2}^{A/Cu}$, which are material dependent indicators. For example, in Rh and Ir, $\delta_{a_0 c_{44}}^{A/Cu}$ and $\delta_{a_0 \mu}^{A/Cu}$ are about two times larger than $\delta_{GB(fit)}^{A/Cu}$.

In high-angle GBs with high energies, the atomic structure near the boundary is less close-packed and many bulk-like bonds are missing which resembles locally a surface-like packing. Exten-

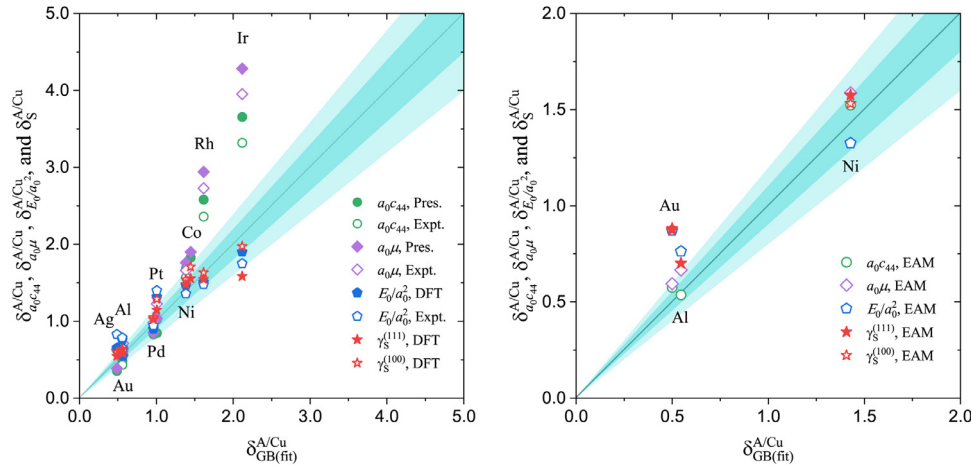


Fig. 3. (Color online) Comparison of $\delta_{GB(fit)}^{A/B}$ with $\delta_{a_0c_{44}}^{A/B}$, $\delta_{a_0\mu}^{A/B}$, $\delta_{E_0/a_0^2}^{A/B}$, and $\delta_S^{A/B}$. For clarity, we show the relevant ratios of parameters from DFT (a) and EAM (b) studies separately. Shaded regions correspond to the deviations within 10% (dark blue) and 20% (light blue), respectively. The EAM and experimental shear moduli are from Refs. [32,77]. The DFT, EAM, and experimental cohesive energies are from Refs. [32,78,79]. The surface energies are from Refs. [37,38]. Numerical values are listed in Tables in SM. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

sive studies of GBs by three dimensional electron back scattering diffraction (EBSD) showed that the most commonly occurring GB plane orientations are correlated with low index, low energy surface planes [80]. Specially, in fcc metals and alloys, GBs are more likely to be terminated by {111} planes than other orientations [81]. In light of these observations, we consider the surface energy of close-packed surface facets as an alternative indicator of the GBEs. A simple physical model for understanding the relation between GBE and surface energy is provided in SM. Indeed, our analysis indicates that the ratio of the low-index surface energies ($\delta_S^{A/B}$) gives a highly accurate prediction of δ . In Fig. 2, the (111) surface energies of pure metals locate approximately on the same lines as the GBEs. For Al, Au, Ag, Ni, Pd, Pt, Co, and Rh, the ratios of the (111) surface energies ($\delta_{S(111)}^{A/Cu}$) are very close the actually slopes of the GBEs ($\delta_{GB(fit)}^{A/Cu}$) with mean deviation of $\sim 9\%$. The largest overestimation is found for Ir, $\sim 25\%$, which is still much better than the prediction based on shear moduli or cohesive energy (Fig. 3). Similar observations apply when using the (001) surface energies, see Table 1.

In polycrystal materials, GBs are normally divided into different categories, i.e., low-angle GBs, high-angle random GBs, and special GBs like $\Sigma 3(111)$ coherent twin [82]. The GBEs of low angle GBs are usually described well by the Shockley-Read type of dislocation model, being a function of the misorientation [83]. The special GBs are often characterized by perfect or high lattice matching, associated with low free energies and shown at the cusps on the γ plots. Particularly, the energy of $\Sigma 3(111)$ coherent twin can be accurately obtained from the measured or calculated stacking fault energy [84]. The GBEs of high-angle GBs are determined as an averaged value obtained directly from experiments examining the thermal groove angles at the GB/surface triple junctions [15,85], or indirectly from Borisov's model based on GB and lattice self-diffusion coefficients [22–24]. From the direct measurements, only representative values of high-angle GBEs are obtained for unspecified GBs [15,85,86], whereas in the indirect measurements, the underlying models suggest that the same GB structures are adopted for all metals (see Refs. [22–24] for details). However, the results from the above two types of experiments agree well with each other for all fcc metals [22,24]. Therefore, we may assume that the same effective GB structures are adopted to describe the general GBs in polycrystal fcc metals (see Notes in SM) and thus we can correlate the formation energies of the general GBs and the surface energies in a similar way as the pure tilt or twist GBs. In Fig. 4, we compare the

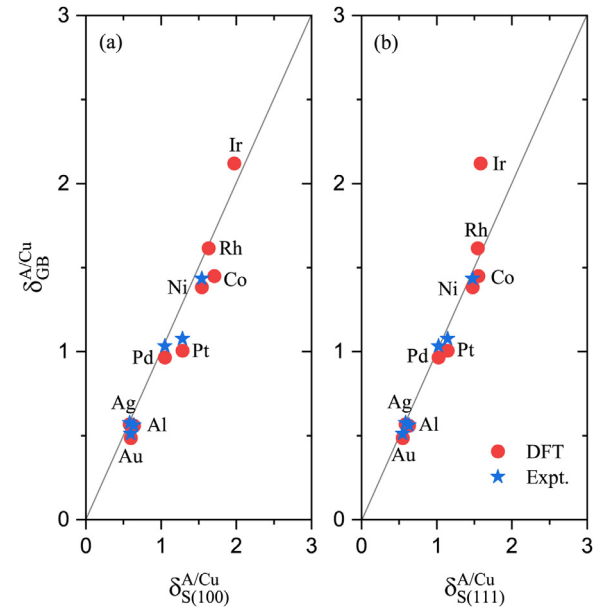


Fig. 4. (Color online) Comparison of the ratio of the GBEs with the ratios of the low-index surface energies, (a) (100) surface and (b) (111) surface, for fcc metals. The ratios of the experimental GBEs (0 K) for the general GBs are also plotted. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

ratio of the experimental GBEs with the DFT calculated gradients ($\delta_{GB(fit)}^{A/B}$) and the ratio of the surface energies ($\delta_{S(111)}^{A/Cu}$ and $\delta_{S(100)}^{A/Cu}$, respectively). A good agreement is reached among these parameters, which justifies the assumption that an effective GB structure exists for the general GBs in isostructural materials. Consequently, the above findings suggest a simple approach for predicting the general GBEs, assuming that GB characteristic distributions are approximately identical in metals with isotropic structures. This speculation is in fact consistent with the experimental observation that isostructural materials have similar GBE anisotropies [6]. We further illustrate the approach by taking Cu as the reference system with measured general GBE of $\gamma_{GB}^{expt,Cu}$. Then the general GBE of an fcc metal A can be predicted as $\gamma_{GB}^A \approx \delta_S^{A/Cu} \times \gamma_{GB}^{expt,Cu}$ where $\delta_S^{A/Cu}$ is the ratio of the surface energies of metal A and Cu. This

ratio changes weakly with temperature up to the room temperature (see discussion in SM) and thus the formula is expected to apply at both low and room temperature. Following this approach, we predicted the 0 K GBEs of all metals considered here. Results are listed in Table 1.

Most importantly, the same approach can be applied to complex alloys for predicting the general GBEs. Here we consider the paramagnetic stainless steel 304 ($\text{Fe}_{0.71}\text{Cr}_{0.20}\text{Ni}_{0.09}$, atomic concentration) as an example, for which the (111) surface energy was calculated to be 2.83 J/m^2 at 0 K [39]. Taking Cu as the reference system again, the ratio of the surface energy $\delta_{\text{S}(111)}^{\text{Fe}_{0.71}\text{Cr}_{0.20}\text{Ni}_{0.09}/\text{Cu}}$ is 2.18 and using the room-temperature general GBE of Cu (0.74 J/m^2 , Ref. [24]), for the general GBE of the 304 stainless steel we predict 1.61 J/m^2 . Our value agrees well with the experimental one of 1.67 J/m^2 reported at room temperature by Murr et al. [85], especially when considering the errors associated with the experimental values, such as the linear temperature dependence and the effects from minor alloying elements. In fact, with the concentration dependent surface energy calculated, we can also provide a parameterized function of predicting the GBE with respect to the chemical variations. Pitkänen et al. [39] provided the regression function for the (111) surface energy with respect to the composition in $\text{Fe}_{1-c-n}\text{Cr}_c\text{Ni}_n$ stainless steel, viz.

$$\gamma_{\text{S}(111)} = 1.279c - 0.143n + 2.588 \text{ (J/m}^2\text{)}, \quad (1)$$

where c and n are the atomic fractions of Cr and Ni contents, respectively. The above formula was established for compositions $0.12 \leq c \leq 0.32$ and $0.04 \leq n \leq 0.32$. Now using the present approach based on surface energies, for the general GBE of $\text{Fe}_{1-c-n}\text{Cr}_c\text{Ni}_n$ alloys we obtain

$$\gamma_{\text{GB}} = 0.727c - 0.081n + 1.471 \text{ (J/m}^2\text{)}. \quad (2)$$

The above linear expression in terms of weight percent (wt.%) becomes

$$\gamma_{\text{GB}} = 0.00766x - 0.00070y + 1.474 \text{ (J/m}^2\text{)}, \quad (3)$$

where x and y are the weight percent of Cr and Ni contents, respectively. The variables are within the limits ($11 \leq x \leq 30$, $4 \leq y \leq 34$, wt.%). Using the measured self-diffusion data, the GBE in $\text{Fe}_{0.71}\text{Cr}_{0.19}\text{Ni}_{0.10}$ at 900°C calculated by Gupta [24] was 0.79 J/m^2 . Assuming a temperature dependence of $-0.89 \text{ mJ/m}^2/\text{K}$ as for the 304 stainless steel [85], the room temperature GBE in this alloy is estimated to be 1.53 J/m^2 , which is also in nice agreement with our predicted value of 1.60 J/m^2 based on Eq. (2). Similarly, in a 316 stainless steel ($\text{Fe}_{0.63}\text{Cr}_{0.18}\text{Ni}_{0.19}$), the experimental GBE at room temperature ($1.54 \sim 1.62 \text{ J/m}^2$), extrapolated from $0.90 \sim 0.98 \text{ J/m}^2$ at 750°C [87] with a linear temperature dependence of $-0.89 \text{ mJ/m}^2/\text{K}$ [85] is also in line with our predicted one (1.59 J/m^2).

In summary, we explored the correlation between the GBEs in fcc metals with *ab initio* calculations. Our results demonstrated that the GBEs in fcc metals are correlated with MAE or RMSE normally less than 0.1 J/m^2 . A material dependent parameter δ is therefore expected to scale the GBEs of the same GB structure in a pair of fcc metals. Here, we found that the ratio of the low-index surfaces are consistent with $\delta_{\text{GB}(\text{fit})}$ obtained from linear fitting of the *ab initio* GBEs for tilt and twist GBs in the studied metals. Using *ab initio* surface energies and the reference experimental data in Cu, we computed the general GBEs in other pure fcc metals and in a complex solid solution alloy with error of $\sim 10\%$. The present work introduces a feasible method for the prediction of the GBEs using *ab initio* calculations. We envision that with more *ab initio* studies for the GBs with structures varying in the space of the five DOFs in a reference metal, using the surface energy-based scaling parameters as proposed in the present work, the GBEs and anisotropy in complex alloys can be readily determined.

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.

Acknowledgments

The present work is performed under the project “SuperFraMat” financed by the Swedish Steel Producers’ Association (Jernkontoret) and the Swedish Innovation Agency (Vinnova). The authors also acknowledge the Swedish Research Council, the Swedish Foundation for Strategic Research, the Swedish Energy Agency, the Hungarian Scientific Research Fund (OTKA 128229), the China Scholarship Council, and the Carl Tryggers Foundation for financial support. The computations were performed on resources provided by the Swedish National Infrastructure for Computing (SNIC) at the National Supercomputer Centre (NSC) in Linköping partially funded by the Swedish Research Council through grant agreement no. 2018-05973.

Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.scriptamat.2021.114118.

References

- [1] A.P. Sutton, R.W. Balluffi, *Interfaces in Crystalline Materials*, Clarendon Press, Oxford, 1995.
- [2] G.S. Rohrer, E.A. Holm, A.D. Rollett, S.M. Foiles, J. Li, D.L. Olmsted, *Acta Mater.* 58 (15) (2010) 5063–5069, doi:10.1016/j.actamat.2010.05.042.
- [3] V. Randle, *Acta Mater.* 52 (14) (2004) 4067–4081, doi:10.1016/j.actamat.2004.05.031.
- [4] V. Randle, G. Owen, *Acta Mater.* 54 (7) (2006) 1777–1783, doi:10.1016/j.actamat.2005.11.046.
- [5] A.R. Krause, P.R. Cantwell, C.J. Marvel, C. Compson, J.M. Rickman, M.P. Harmer, *J. Am. Ceram. Soc.* 102 (2) (2019) 778–800, doi:10.1111/jace.16045.
- [6] G.S. Rohrer, *J. Mater. Sci.* 46 (18) (2011) 5881–5895, doi:10.1007/s10853-011-5677-3.
- [7] V.V. Bulatov, B.W. Reed, M. Kumar, *Acta Mater.* 65 (2014) 161–175, doi:10.1016/j.actamat.2013.10.057.
- [8] C. Herring, *The Physics of Powder Metallurgy*, McGraw Hill, New York, 1951.
- [9] J. Kudrman, J. Čadek, *Czech. J. Phys. B* 19 (11) (1969) 1337–1342, doi:10.1007/BF01690833.
- [10] C.S. Smith, *Trans. Metall. Soc. AIME* 175 (1948) 15–51.
- [11] N.A. Gjostein, F.N. Rhines, *Acta Metall.* 7 (5) (1959) 319–330, doi:10.1016/0001-6160(59)90198-1.
- [12] G.C. Hasson, C. Goux, *Scr. Mater.* 5 (10) (1971) 889–894, doi:10.1016/0036-9748(71)90064-0.
- [13] H. Mykura, *Acta Metall.* 3 (5) (1955) 436–441, doi:10.1016/0001-6160(55)90131-0.
- [14] L.E. Murr, R.J. Horylev, W.N. Lin, *Philos. Mag.* 22 (177) (1970) 515–542, doi:10.1080/14786437008225841.
- [15] T.A. Roth, *Mater. Sci. Eng.* 18 (2) (1975) 183–192, doi:10.1016/0025-5416(75)90168-8.
- [16] G.F. Bolling, *Acta Metall.* 16 (9) (1968) 1147–1157, doi:10.1016/0001-6160(68)90049-7.
- [17] L.E. Murr, *Acta Metall.* 21 (6) (1973) 791–797, doi:10.1016/0001-6160(73)90043-6.
- [18] W.R. Tyson, W.A. Miller, *Surf. Sci.* 62 (1) (1977) 267–276, doi:10.1016/0039-6028(77)90442-3.
- [19] F.R. De Boer, W.C.M. Mattens, R. Boom, A.R. Miedema, A.K. Niessen, *Cohesion in Metals*, North-Holland, Amsterdam, 1988.
- [20] L. Vitos, A.V. Ruban, H.L. Skriver, J. Kollar, *Surf. Sci.* 411 (1–2) (1998) 186–202, doi:10.1016/S0039-6028(98)00363-X.
- [21] V.T. Borisov, V.M. Golikov, G.V. Scherbedinskiy, *Phys. Met. Metall.* 17 (1964) 881–885.
- [22] J. Pelleg, *Philos. Mag.* 14 (129) (1966) 595–601, doi:10.1080/14786436608211954.
- [23] D. Gupta, *Philos. Mag.* 33 (1) (1976) 189–197, doi:10.1080/14786437608221103.
- [24] D. Gupta, *Metall. Trans. A* 8 (9) (1977) 1431–1438, doi:10.1007/BF02642856.
- [25] D. Prokoshkina, V.A. Esin, G. Wilde, S.V. Divinski, *Acta Mater.* 61 (14) (2013) 5188–5197, doi:10.1016/j.actamat.2013.05.010.
- [26] J.D. Rittner, D.N. Seidman, *Phys. Rev. B* 54 (10) (1996) 6999, doi:10.1103/PhysRevB.54.6999.

- [27] D. Wolf, *Acta Metall.* 37 (7) (1989) 1983–1993, doi:[10.1016/0001-6160\(89\)90082-5](https://doi.org/10.1016/0001-6160(89)90082-5).
- [28] D. Wolf, S. Phillpot, *Mater. Sci. Eng. A* 107 (1989) 3–14, doi:[10.1016/0921-5093\(89\)90370-5](https://doi.org/10.1016/0921-5093(89)90370-5).
- [29] D. Udler, D.N. Seidman, *Phys. Rev. B* 54 (16) (1996) R11133, doi:[10.1103/PhysRevB.54.R11133](https://doi.org/10.1103/PhysRevB.54.R11133).
- [30] M. Shiga, M. Yamaguchi, H. Kaburaki, *Phys. Rev. B* 68 (24) (2003) 245402, doi:[10.1103/PhysRevB.68.245402](https://doi.org/10.1103/PhysRevB.68.245402).
- [31] M.A. Tschopp, D.L. McDowell, *Philos. Mag.* 87 (25) (2007) 3871–3892, doi:[10.1080/14786430701455321](https://doi.org/10.1080/14786430701455321).
- [32] E.A. Holm, D.L. Olmsted, S.M. Foiles, *Scr. Mater.* 63 (9) (2010) 905–908, doi:[10.1016/j.scriptamat.2010.06.040](https://doi.org/10.1016/j.scriptamat.2010.06.040).
- [33] D.L. Olmsted, S.M. Foiles, E.A. Holm, *Acta Mater.* 57 (13) (2009) 3694–3703, doi:[10.1016/j.actamat.2009.04.007](https://doi.org/10.1016/j.actamat.2009.04.007).
- [34] H. Zheng, X.G. Li, R. Tran, C. Chen, M. Horton, D. Winston, K.A. Persson, S.P. Ong, *Acta Mater.* 186 (2020) 40–49, doi:[10.1016/j.actamat.2019.12.030](https://doi.org/10.1016/j.actamat.2019.12.030).
- [35] D. Scheiber, R. Pippin, P. Puschnig, L. Romaner, *Model. Simul. Mat. Sci. Eng.* 24 (3) (2016) 035013, doi:[10.1088/0965-0393/24/3/035013](https://doi.org/10.1088/0965-0393/24/3/035013).
- [36] J.L. Wang, G.K.H. Madsen, R. Drautz, *Model. Simul. Mat. Sci. Eng.* 26 (2) (2018) 025008, doi:[10.1088/1361-651X/aa9f81](https://doi.org/10.1088/1361-651X/aa9f81).
- [37] J.Y. Lee, M.P.J. Punkkinen, S. Schönecker, Z. Nabi, K. Kádas, V. Zólyomi, Y.M. Koo, Q.M. Hu, R. Ahuja, B. Johansson, et al., *Surf. Sci.* 674 (2018) 51–68, doi:[10.1016/j.susc.2018.03.008](https://doi.org/10.1016/j.susc.2018.03.008).
- [38] J.C.W. Swart, P. van Helden, E. van Steen, *J. Phys. Chem. C* 111 (13) (2007) 4998–5005, doi:[10.1021/jp0684980](https://doi.org/10.1021/jp0684980).
- [39] H. Pitkänen, M. Alatalo, A. Puisto, M. Ropo, K. Kokko, L. Vitos, *Surf. Sci.* 609 (2013) 190–194, doi:[10.1016/j.susc.2012.12.007](https://doi.org/10.1016/j.susc.2012.12.007).
- [40] W. Kohn, L.J. Sham, *Phys. Rev.* 140 (4A) (1965) A1133, doi:[10.1103/PhysRev.140.A1133](https://doi.org/10.1103/PhysRev.140.A1133).
- [41] P.E. Blöchl, *Phys. Rev. B* 50 (24) (1994) 17953, doi:[10.1103/PhysRevB.50.17953](https://doi.org/10.1103/PhysRevB.50.17953).
- [42] J.P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* 77 (18) (1996) 3865, doi:[10.1103/PhysRevLett.77.3865](https://doi.org/10.1103/PhysRevLett.77.3865).
- [43] T. Nishiyama, A. Seko, I. Tanaka, *Phys. Rev. Mater.* 4 (12) (2020) 123607, doi:[10.1103/PhysRevMaterials.4.123607](https://doi.org/10.1103/PhysRevMaterials.4.123607).
- [44] H. Hallberg, P.A.T. Olsson, *J. Mech. Phys. Solids* 90 (2016) 160–178, doi:[10.1016/j.jmps.2016.02.026](https://doi.org/10.1016/j.jmps.2016.02.026).
- [45] J. Xu, J.B. Liu, S.N. Li, B.X. Liu, Y. Jiang, *Phys. Chem. Chem. Phys.* 18 (27) (2016) 17930–17940, doi:[10.1039/C6CP02505F](https://doi.org/10.1039/C6CP02505F).
- [46] J.J. Bean, K.P. McKenna, *Acta Mater.* 110 (2016) 246–257, doi:[10.1016/j.actamat.2016.02.040](https://doi.org/10.1016/j.actamat.2016.02.040).
- [47] Q. Gao, M. Widom, *Phys. Rev. B* 90 (14) (2014) 144102, doi:[10.1103/PhysRevB.90.144102](https://doi.org/10.1103/PhysRevB.90.144102).
- [48] T. Tsuru, Y. Kaji, D. Matsunaka, Y. Shibutani, *Phys. Rev. B* 82 (2) (2010) 024101, doi:[10.1103/PhysRevB.82.024101](https://doi.org/10.1103/PhysRevB.82.024101).
- [49] R.Z. Wang, M. Kohyama, S. Tanaka, T. Tamura, S. Ishibashi, *Mater. Trans.* 50 (1) (2009) 11–18, doi:[10.2320/matertrans.MD200820](https://doi.org/10.2320/matertrans.MD200820).
- [50] H. Miura, M. Kato, T. Mori, *J. Mater. Sci. Lett.* 13 (1) (1994) 46–48, doi:[10.1007/BF02352916](https://doi.org/10.1007/BF02352916).
- [51] T. Uesugi, K. Higashi, *J. Mater. Sci.* 46 (12) (2011) 4199–4205, doi:[10.1007/s10853-011-5305-2](https://doi.org/10.1007/s10853-011-5305-2).
- [52] R. Mahjoub, K.J. Laws, N. Stanford, M. Ferry, *Acta Mater.* 158 (2018) 257–268, doi:[10.1016/j.actamat.2018.07.069](https://doi.org/10.1016/j.actamat.2018.07.069).
- [53] M. Yamaguchi, K.I. Ebihara, M. Itakura, T. Tsuru, K. Matsuda, H. Toda, *Comput. Mater. Sci.* 156 (2019) 368–375, doi:[10.1016/j.commatsci.2018.10.015](https://doi.org/10.1016/j.commatsci.2018.10.015).
- [54] Y. Inoue, T. Uesugi, Y. Takigawa, K. Higashi, *Mater. Sci. Forum* 561 (2007) 1837–1840. [10.4028/www.scientific.net/MSF.561-565.1837](https://doi.org/10.4028/www.scientific.net/MSF.561-565.1837)
- [55] T. Tsuru, Y. Shibutani, Y. Kaji, *Phys. Rev. B* 79 (1) (2009) 012104, doi:[10.1103/PhysRevB.79.012104](https://doi.org/10.1103/PhysRevB.79.012104).
- [56] F.H. Cao, Y. Jiang, T. Hu, D.F. Yin, *Philos. Mag.* 98 (6) (2018) 464–483, doi:[10.1080/14786435.2017.1408968](https://doi.org/10.1080/14786435.2017.1408968).
- [57] X.Y. Pang, N. Ahmed, R. Janisch, A. Hartmaier, *J. Appl. Phys.* 112 (2) (2012) 023503, doi:[10.1063/1.4736525](https://doi.org/10.1063/1.4736525).
- [58] R. Janisch, N. Ahmed, A. Hartmaier, *Phys. Rev. B* 81 (18) (2010) 184108, doi:[10.1103/PhysRevB.81.184108](https://doi.org/10.1103/PhysRevB.81.184108).
- [59] A.F. Wright, S.R. Atlas, *Phys. Rev. B* 50 (20) (1994) 15248, doi:[10.1103/PhysRevB.50.15248](https://doi.org/10.1103/PhysRevB.50.15248).
- [60] D.I. Thomson, V. Heine, M.W. Finnis, N. Marazi, *Philos. Mag. Lett.* 76 (4) (1997) 281–288, doi:[10.1080/095008397179039](https://doi.org/10.1080/095008397179039).
- [61] D.I. Thomson, V. Heine, M.C. Payne, N. Marzari, M.W. Finnis, *Acta Mater.* 48 (14) (2000) 3623–3632, doi:[10.1016/S1359-6454\(00\)00175-0](https://doi.org/10.1016/S1359-6454(00)00175-0).
- [62] J. Chen, A.M. Dongare, *J. Mater. Sci.* 52 (1) (2017) 30–45, doi:[10.1007/s10853-016-0389-3](https://doi.org/10.1007/s10853-016-0389-3).
- [63] Z.L. Pan, V. Borovikov, M.I. Mendelev, F. Sansoz, *Model. Simul. Mat. Sci. Eng.* 26 (7) (2018) 075004, doi:[10.1088/1361-651X/aadea3](https://doi.org/10.1088/1361-651X/aadea3).
- [64] D.J. Siegel, J.C. Hamilton, *Acta Mater.* 53 (1) (2005) 87–96, doi:[10.1016/j.actamat.2004.09.006](https://doi.org/10.1016/j.actamat.2004.09.006).
- [65] O.M. Løvvik, D.D. Zhao, Y.J. Li, R. Bredesen, T. Peters, *Membranes* 8 (3) (2018) 81, doi:[10.3390/membranes8030081](https://doi.org/10.3390/membranes8030081).
- [66] C.J. O'Brien, C.M. Barr, P.M. Price, K. Hattar, S.M. Foiles, *J. Mater. Sci.* 53 (4) (2018) 2911–2927, doi:[10.1007/s10853-017-1706-1](https://doi.org/10.1007/s10853-017-1706-1).
- [67] S. Ratanaphan, D.L. Olmsted, V.V. Bulatov, E.A. Holm, A.D. Rollett, G.S. Rohrer, *Acta Mater.* 88 (2015) 346–354, doi:[10.1016/j.actamat.2015.01.069](https://doi.org/10.1016/j.actamat.2015.01.069).
- [68] S.I. Prokofiev, *J. Mater. Sci.* 52 (8) (2017) 4265–4277, doi:[10.1007/s10853-016-0681-2](https://doi.org/10.1007/s10853-016-0681-2).
- [69] S.V. Divinski, G. Reglitz, G. Wilde, *Acta Mater.* 58 (2) (2010) 386–395, doi:[10.1016/j.actamat.2009.09.015](https://doi.org/10.1016/j.actamat.2009.09.015).
- [70] A.R. Miedema, *Z. Metallk.* 69 (5) (1978) 287–292.
- [71] R. Birringer, M. Hoffmann, P. Zimmer, *Phys. Rev. Lett.* 88 (20) (2002) 206104, doi:[10.1103/PhysRevLett.88.206104](https://doi.org/10.1103/PhysRevLett.88.206104).
- [72] R. Birringer, M. Hoffmann, P. Zimmer, *Z. Metallk.* 94 (10) (2003) 1052–1061, doi:[10.3139/146.031052](https://doi.org/10.3139/146.031052).
- [73] M. McLean, E.D. Hondros, *J. Mater. Sci.* 6 (1) (1971) 19–24, doi:[10.1007/BF00550286](https://doi.org/10.1007/BF00550286).
- [74] E.D. Hondros, *Sci. Prog.* 68 (269) (1982) 35–63.
- [75] W.T. Read, W. Shockley, *Phys. Rev.* 78 (3) (1950) 275, doi:[10.1103/PhysRev.78.275](https://doi.org/10.1103/PhysRev.78.275).
- [76] D. Wolf, *J. Appl. Phys.* 68 (7) (1990) 3221–3236, doi:[10.1063/1.346373](https://doi.org/10.1063/1.346373).
- [77] G. Simons, H. Wang, *J. Grand. Res. Center* 34 (1) (1977) 269.
- [78] R. Nazarov, T. Hickel, J. Neugebauer, *Phys. Rev. B* 85 (14) (2012) 144118, doi:[10.1103/PhysRevB.85.144118](https://doi.org/10.1103/PhysRevB.85.144118).
- [79] C. Kittel, *Introduction to Solid State Physics*, Wiley, New York, 1976.
- [80] G.S. Rohrer, J. Li, S. Lee, A.D. Rollett, M. Groeber, M.D. Uchic, *Mater. Sci. Technol.* 26 (6) (2010) 661–669, doi:[10.1179/026708309X12468927349370](https://doi.org/10.1179/026708309X12468927349370).
- [81] H. Beladi, N.T. Nuhfer, G.S. Rohrer, *Acta Mater.* 70 (2014) 281–289, doi:[10.1016/j.actamat.2014.02.038](https://doi.org/10.1016/j.actamat.2014.02.038).
- [82] , *Metall. Trans. B* 13 (4) (1982) 527–553, doi:[10.1007/BF02650011](https://doi.org/10.1007/BF02650011).
- [83] A. Otsuki, *J. Mater. Sci.* 40 (12) (2005) 3219–3223, doi:[10.1007/s10853-005-2688-y](https://doi.org/10.1007/s10853-005-2688-y).
- [84] X. Sun, S. Lu, R. Xie, X. An, W. Li, T. Zhang, C. Liang, X. Ding, Y. Wang, H. Zhang, L. Vitos, *Mater. Des.* 199 (2021) 109396, doi:[10.1016/j.matdes.2020.109396](https://doi.org/10.1016/j.matdes.2020.109396). <https://www.sciencedirect.com/science/article/pii/S0264127520309321>
- [85] L.E. Murr, G.I. Wong, R.J. Horylev, *Acta Metall.* 21 (5) (1973) 595–604, doi:[10.1016/0001-6160\(73\)90068-0](https://doi.org/10.1016/0001-6160(73)90068-0).
- [86] M. McLean, *J. Mater. Sci.* 8 (4) (1973) 571–576, doi:[10.1007/BF00550462](https://doi.org/10.1007/BF00550462).
- [87] R.A. Varin, *Mater. Sci. Eng.* 66 (1) (1984) 97–105, doi:[10.1016/0025-5416\(84\)90144-7](https://doi.org/10.1016/0025-5416(84)90144-7).