

R. Kirchheim: On the solute-defect interaction in the framework of a defactant concept

Reiner Kirchheim

Georg-August-Universität Göttingen, Göttingen, Germany

On the solute-defect interaction in the framework of a defactant concept

Dedicated to Professor Dr. Günter Gottstein on the occasion of his 65th birthday

It will be shown that there is an analogy between surfactants in liquids which stabilize structures with large surface areas such as foams or microemulsions, and certain components in a crystalline solid, which stabilize defects such as grain boundaries and dislocations. These components are then called defactants. In the presence of defactants microstructural changes may occur because some of the defects compete more successfully for segregation of the defactants than others. Thus voids are formed at grain boundaries of Cu–Bi alloys because the formation energy of voids is provided by the interaction energy of Bi-atoms of the newly created surface. Or the beneficial role of rhenium on the high temperature creep of superalloys may be interpreted as a deficiency of defactants stabilizing dislocations and/or vacancies. These examples are discussed in the present work after a general treatment of the role of defactants.

Keywords: Solute-defect interaction; Segregation; Gibbs adsorption isotherm

1. Introduction

It is well known that surfactant molecules reduce the surface tension of water because the molecules contain a hydrophilic and a hydrophobic part. Therefore, they are enriched at the surface sticking their hydrophobic part out of the water and the more they segregate the more the surface energy γ is reduced. This relationship was treated quantitatively by

Gibbs [1] leading to the Gibbs Adsorption Isotherm

$$d\gamma = -\Gamma_A d\mu_A \quad (1)$$

where μ_A is the chemical potential of the surfactant labelled A and Γ_A is its excess at the surface. Equation 1 was also used for phase- and grain boundaries, because for them Gibbs' procedure of cutting out a large enough volume around the interface and assuming that the remaining parts of the sample are not affected by the interface is applicable as well. This way the total free energy of the interface is calculated and the excess is independent of the interfacial area. The evaluation of the excess Γ_A requires a well defined positioning of the geometrical interface or an elaborate mathematical treatment [2].

Wagner [3] proposed a different evaluation of the excess solute which differs from the Gibbs one slightly as it leads to a differential excess as shown in this study. It has also been shown by the present author that Wagner's treatment can be extended to other crystalline defects such as dislocations and vacancies yielding the same Eq. (1) [4, 5]. In the generalized form of Eq. (1) γ stands for the free energy of the defect formation. The Gibbs procedure fails in the case of dislocations as they have a long range strain field and, therefore, the separation into two volumes with one containing the dislocation and the other not being affected by it is not applicable. In crystalline solids one has to distinguish between surfaces with different orientations, different grain boundaries with different orientation and the orientation difference of the adjacent grains and differ-

ent dislocations with different Burgers and line vectors. Thus a large variety of defects may be present in a solid giving rise to a corresponding large number of equations of type Eq. (1).

Components of a material which segregate to a defect lead to a positive excess ($\Gamma_A > 0$) and via Eq. (1) reduce the defect energy. In analogy to a surfactant (*surface acting agent*) reducing the surface energy these components will be called defactants (*defect acting agent*) in the following. It will be shown that surfaces may be considered as a type of defect and, therefore, surfactants are a subgroup of defactants.

For defactant A ($\Gamma_A > 0$) Eq. (1) predicts a steady decrease in the defect formation energy and the intriguing question arises whether this may lead to negative formation energies. Consequences of negative γ values for crystalline alloys are discussed in Refs. [4, 5]. These considerations are independent of the material and, therefore, are a subject of controversial discussion in various areas. Thus, breathing of many animals which requires a large increase in the internal surface of the lungs is facilitated by phospholipids in cooperation with other surfactants because they reduce the surface energy of the aqueous films in the alveolus to very low values [6]. Whether these values may be zero as concluded from the exceptional stability of foams formed from a liquid of the human lungs is controversial [6]. In microemulsions however the phase boundary between water and oil phase reaches values which are several orders of magnitude smaller compared to the surfactant free case [7] and, therefore, may be set equal to zero.

In the following the derivation of the generalized Eq. (1) is repeated in order to establish a more general formalism with novel or corrected arguments when compared with the original work [4] and to provide the background for understanding the action of defactants as exemplified for some of the effects which were not treated in Ref. [5].

2. General formal treatment

Following Wagner [3] the thermodynamic state function Φ is introduced

$$\Phi = F - n_A \mu_A \quad (2)$$

where F is Helmholtz free energy and n_A the number of moles of component A. Eq. (2) has the differential

$$d\Phi = p dV - S dT + V \gamma d\rho + \mu_B dn_B - n_A d\mu_A \quad (3)$$

with p , V , T and S have their usual meaning, n_B and μ_B are the number of moles of component B or its chemical potential, respectively. In addition, Eq. (3) contains a work term $V \gamma d\rho$ due to the defect density ρ and the free energy of defect formation γ . This is different to Wagner [3] who was treating the special case of surfaces of area a only, with the corresponding work term γda . With the general work term Eq. (2) includes all kinds of defects, where ρ may be interfacial area a per volume V or dislocation length l per volume V or number of point defects n per volume V . Within the framework of this generalization even the surface or a phase boundary becomes a defect. The term may be justified by the fact that the continuum will be interrupted there. Vacancies or point defects in general are special defects because their generation is accompanied by a much larger en-

tropy gain when compared with extended defects and, therefore, they become equilibrium defects being generated up to a concentration where their free energy of formation becomes zero.

The function Φ is appropriate for measurements with constant volume, constant temperature and in a closed system with respect to solvent atoms B but open under constant chemical potential with respect to solute atom A . As second derivatives of state functions are independent of the sequence of differentiation, we obtain the following Maxwell relation

$$\frac{\partial^2 \Phi}{\partial \mu_A \partial \rho} = - \frac{\partial n_A}{\partial \rho} \Big|_{V, T, \mu_A, n_B} = \frac{\partial^2 \Phi}{\partial \rho \partial \mu_A} = \frac{\partial \gamma}{\partial \mu_A} \Big|_{V, T, \rho, n_B} \quad (4)$$

Using Wagner's definition of excess solute A

$$\Gamma_A \equiv \frac{1}{V} \frac{\partial n_A}{\partial \rho} \Big|_{V, T, \mu_A, n_B} \quad (5)$$

in Eq. (4) leads to

$$\frac{\partial \gamma}{\partial \mu_A} \Big|_{V, T, \rho, n_B} = -\Gamma_A \quad (6)$$

which is equivalent to Gibbs' Adsorption Equation if a is replaced by ρ . Conditions under which the excess can be measured are given by Eq. (5), i.e. the number of moles δn_A entering the system from a reservoir after a change of defect density $\delta \rho$ has to be determined while V , T , μ_A and n_B have to be kept constant corresponding to a closed system regarding component B and open regarding A. This is exemplified in Fig. 1 based on a Gedankenexperiment by Wagner [3].

The definition of excess as given by Eq. (5) is a differential quantity whereas Gibbs' [1] and Cahn's [2] definition yields an integral excess. Wagner [3] did not distinguish between the two by assuming that the surface excess is proportional to the surface area. Thus he was able to prove the equivalence of his and Gibbs' treatment. However, in discussing the problem of negative defect energies in the following chapter a distinction between differential and integral excess has to be made.

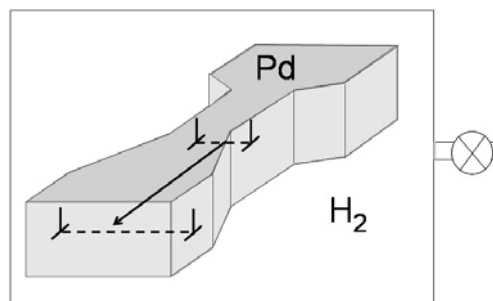


Fig. 1. Wagner's Gedankenexperiment [3] modified for dislocations. A vessel with a closed valve contains a dog bone shaped single crystal of palladium and gaseous H_2 . By an external force (e.g. shear stress) the dislocation is moved from the thin to the thick region. Thus the dislocation length is increased and the excess hydrogen from the newly generated part of the defect is absorbed from the gas phase. Thereby the partial pressure of H_2 is decreased and the number of moles of H per additional dislocation length, which have to be added via the valve, in order to establish the initial H_2 pressure, is defined as excess hydrogen.

3. Negative free energies of defect formation

Integrating Eq. (6) yields γ as a function of the chemical potential μ_A and the result is presented schematically in Fig. 2. For $\mu_A \rightarrow -\infty$ the concentration of defectant A will approach zero and $\Gamma_A \rightarrow 0$ yielding zero slope according to Eq. (6). Raising μ_A to the value of the interaction energy between defect and defectant, H_s , leads to an increasing positive excess. If the excess saturates, for example by forming a monolayer of defectants at a grain boundary, γ decreases linearly with increasing μ_A and may finally become negative (case 1 in Fig. 2, for simplicity the term defect energy instead of free energies of defect formation will be used in the following). Despite of increasing defectant concentrations the chemical potential where γ changes sign may not be reached because an A-rich phase precipitates (case 3 in Fig. 2). Such behaviour is experimentally observed for most surfactants in aqueous solution [8], where the surfactant molecules form micelles, i. e. a kind of precipitate. This seemed also to be the case for grain boundary segregation in polycrystals as shown in Ref. [9].

Let us assume in the following that case 1 in Fig. 2 with negative defect energies may be realised. Then the system lowers its overall energy by increasing the defect density ρ . Thus surfaces and interfaces become unstable as can be shown in computer simulations [10]. The increasing defect density has different consequences for closed ($dn_B = 0$ and $dn_A = 0$) and partially open ($dn_B = 0$) systems.

In a closed system and for $\gamma < 0$ defects will be generated and the newly formed have to be decorated with solute A to get the same excess Γ_A as the older defects. Thus the surrounding matrix is depleted with respect to the defectant A and, therefore, its chemical potential decreases and γ increases according to Eq. (6) and/or Fig. 2. These processes

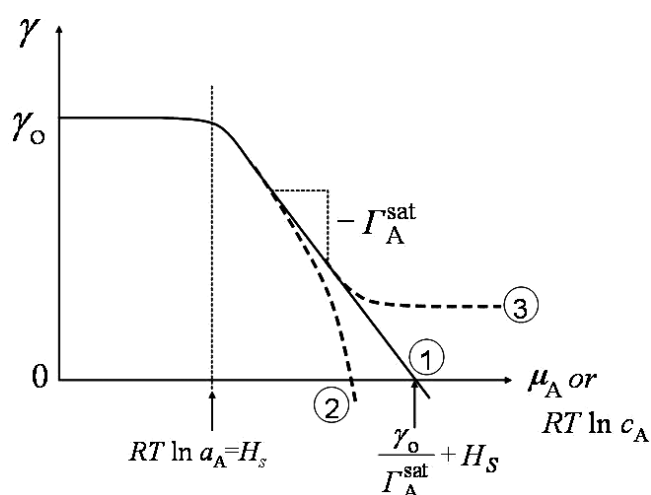


Fig. 2. Schematic dependence of the defect energy, γ , on the chemical potential, μ_A of solute A according to Eq. (1) or (5), respectively. At low chemical potentials or activities the excess A, Γ_A , is negligible and the slope of the curve is zero. If the chemical potential reaches the interaction energy, H_s , of A with the defect, the excess increases and the slope becomes negative. Saturating the defect with Γ_A^{sat} leads to a constant slope (line 1) which intercepts the abscissa at the given chemical potential. If the excess does not saturate line 2 describes the expected dependency. Line 3 describes the behaviour, if a new A-rich phase is formed and the logarithm of concentration, c_A , instead of the chemical potential is used as the variable for the abscissa. In the latter case the chemical potential and, therefore, the excess and γ remain constant during the phase separation despite increasing concentration.

continue until $\gamma = 0$. For the case of $\gamma > 0$ defects will be annihilated releasing the defectants to the surrounding matrix. Then the chemical potential μ_A increases and the defect energy of the remaining defects decreases until $\gamma = 0$. Thus in a closed system the state of $\gamma = 0$ can be reached from both sides of positive and negative defect energies and, therefore, represents a metastable equilibrium. The same result was obtained in Ref. [4] by false assumptions which were compensated by a sign error [11].

For $\gamma < 0$ defects will be generated in a partially open system, too; but now the required defectants are delivered from a reservoir ($d\mu_A = \text{const}$). It was shown in Ref. [4] that the attainment of metastable equilibrium in this case requires that

$$\frac{\partial \gamma}{\partial \rho} > 0 \quad (7)$$

i. e. γ has to increase during defect production. Then a state with $\gamma = 0$ and a metastable equilibrium with a constant defect density ρ is attained, where defect production stops because the driving force for this process became zero. In order to show that the state is metastable it is assumed that the system due to fluctuations makes an excursion to slightly positive values of γ . Then annihilation of defects becomes possible, i. e. ρ decreases and due to Eq. (7) γ decreases to zero or to negative values and, therefore, defect annihilation will be stopped or reversed and the system returns to the state with $\gamma = 0$.

For isolated defects not interacting with each other in a direct or indirect way the creation of an additional defect is independent of the defect density and, therefore, the derivative in Eq. (7) should be zero. However, for a negative value of γ the defect density ρ increases with a concomitant decrease in the spatial distance between defects until they finally interact with each other and $\partial \gamma / \partial \rho \neq 0$. Then the following three cases can be distinguished for $\gamma < 0$:

1. The chemical potential of defectants where γ is negative cannot be reached because defectants precipitate.
2. For $\partial \gamma / \partial \rho > 0$ defects are generated up to a density where $\gamma = 0$.
3. For $\partial \gamma / \partial \rho < 0$ defects are generated until the system becomes amorphous.

Case 1 applies for surfactants in water at the critical micelle concentration [8] or for grain boundaries in solids following the Hondros–Seah correlation between terminal solubility and segregation [9]. Case 2 is always fulfilled for vacancies due to their large configurational entropy as shown in Ref. [4]. Another example of case 2 was discussed in Ref. [4] for surface segregation of hydrogen on aluminium oxide as obtained from first principle calculations [12]. It may apply to microemulsions where the droplets of dispersed water or oil phase may become so small that due to the large curvature of their interface boundary or the short distance between adjacent boundaries Eq. (7) becomes valid. In other words a further increase in the total oil/water phase boundary with the concomitant decrease in droplet size requires more energy per area than for coarser emulsions. For surfactant water systems the formation of foams may be stopped because the water films become so thin that surfactants on adjacent surfaces of the film interact and then γ may fulfil Eq. (7). The production of superabundant vacancies in metals with hydrogen as a defectant was realized

by Fukai [13] leading to very high concentrations of up to 10 to 30 at.%. Then the distance between nearest neighbour vacancies is close to the lattice constant. For vacancies the configurational entropy being part of γ has to be taken into account, too. For case 3 no convincing example has been found by the author. From an experimental point of view it may be difficult to differentiate between cases 2 and 3 because the metastable defect density for case 2 may be so high that it cannot be distinguished experimentally from the amorphous state. The discussion of all these cases applies to open systems; for closed systems a depletion of defectants may stop defect formation as discussed before.

4. Defactants and microstructure

In liquids surfaces are the only defects present and Eqs. (3)–(6) are appropriate. But as mentioned before crystals contain various groups of defects. Within the group of one and two dimensional defects one has to distinguish between the various orientations of the defects. Defects of zero dimension, i.e. vacancies in intermetallic compounds will be different depending on their position in the unit cell. The number of all of these distinguishable defects may be L . In order to discuss real or complex crystalline systems containing these L defects and M different components A_m Eqs. (3), (5) and (6) are rewritten as follows:

$$d\Phi = p dV - S dT + V \sum_{l=1}^L \gamma_l d\rho_l + \mu_B dn_B - \sum_{m=1}^M n_{Am} d\mu_{Am}$$

$$\text{with } \Phi = F - \sum_{m=1}^M n_{Am} \mu_{Am} \quad (8)$$

$$F_{lAm} \equiv \frac{1}{V} \left. \frac{\partial n_{Am}}{\partial \rho_l} \right|_{V, T, \mu_{Am}, \rho_{i \neq l} n_B} \quad (9)$$

$$\left. \frac{\partial \gamma_l}{\partial \mu_{Am}} \right|_{V,T,\rho_l,\mu_{Ai \neq m}, n_B} = -\Gamma_{lAm} \quad (10)$$

The vector $\rho_l (l = 1 \text{ to } L)$ may be considered as a representative of the microstructure of a crystalline solid which describes the distribution of defects. But it does not describe the spatial arrangement of the defects. In addition, it may be difficult experimentally to realize the condition in Eq. (9) of changing ρ_l but keeping the density of the other defects $\rho_{i \neq l}$ constant; e. g. dislocation leaving the sample at the surface produce surface steps and reducing grain boundary area is accompanied by the annihilation of triple lines etc. In the following these complications are avoided and the two simplest cases of (i) two defactants interacting with one defect and (ii) two defects interacting with one defactant are discussed in general and ascribed to two interesting phenomena.

5. Two components competing for one defect or the rhenium-effect in superalloys

The ternary alloy B–A1–A2 and one defect of density ρ will be considered. For constant temperature, volume and number of B-atoms Eq. (10) yield

$$d\gamma = -\Gamma_{A1} d\mu_{A1} - \Gamma_{A2} d\mu_{A2} \quad (11)$$

If both components are defectants ($\Gamma_{A1} > 0$, $\Gamma_{A2} > 0$) an increase in their chemical potentials leads to a decrease in γ . This may give rise to higher defect density during a thermo-mechanical treatment of a material. Thus a high density of grain boundaries may be achieved with its beneficial effect on the yield stress. However, for decreasing rates of vacancy creep it may be necessary to decrease the vacancy density or increase their formation energy γ . Then Eq. (11) should give a positive value which can be realized in several ways:

1. $\Gamma_{A1} > 0, \Gamma_{A2} > 0$ (A1 and A2 are defactants), $d\mu_{A1} < 0$ and $d\mu_{A2} < 0$,
2. $\Gamma_{A1} > \Gamma_{A2} > 0$, (A1 and A2 are defactants) $d\mu_{A1} < 0$ and $d\mu_{A2} > 0$ but $-\Gamma_{A1} d\mu_{A1} > \Gamma_{A2} d\mu_{A2}$,
3. $\Gamma_{A1} < 0, \Gamma_{A2} < 0$ (A1 and A2 are anti-defactants), $d\mu_{A1} > 0$ and $d\mu_{A2} > 0$,
4. $\Gamma_{A1} < 0, \Gamma_{A2} > 0$, (A1 is an anti-defactant, A2 is a defactant) $d\mu_{A1} > 0$ and $d\mu_{A2} < 0$.

Cases 1 and 3 are trivial and will not be considered further because usually during alloy engineering one component is partially substituted by another one and, therefore, $d\mu_{A1}$ and $d\mu_{A2}$ have different signs. Thus for decreasing the defect density the conditions given for cases 2 and 4 have to be fulfilled. These cases will be applied for providing a novel explanation of the "rhenium-effect" in superalloys.

Rhenium in single-crystal superalloys has a beneficial effect on the creep resistance of these alloys, which are used in the high temperature parts of gas turbines [14]. At elevated temperatures creep in these alloys is believed to occur by dislocation motion [15]. By adding rhenium to the nickel-base alloys other constituents are replaced and cases 2 and 4 may apply. This will promote creep resistance if the rate determining step is dislocation generation or if the rate determining step is dislocation climb. In the first case the formation energy either due to case 2 or 4 is increased and in the second case the formation energy of vacancies assisting climb is increased leading to lower vacancy concentrations. A third explanation of the rhenium-effect could be a decrease in dislocation mobility, if this is controlled by double-kink formation. Then kinks are the defects and the various defactants and anti-defactants are affecting its formation energy. Again cases 2 and 4 would increase kink formation energies and, therefore, retard dislocation motion. Finally, a fourth possibility may be different solute drag on dislocations. Then rhenium should affect the total excess solute at dislocations. This is a complicated process as both positive and negative excess decreases dislocation mobility. In addition, at elevated temperature solute drag may not play an important role.

6. Defects competing for one defectant or void formation at grain boundaries

For two defects with densities ρ_1 and ρ_2 in a binary alloy (B being the matrix component and A being an alloying addition) Eq. 10 yield

$$d\gamma_1 = -\Gamma_{1A} d\mu_A \quad \text{and} \quad d\gamma_2 = -\Gamma_{2A} d\mu_A \quad (12)$$

Assuming that A-atoms have a larger binding energy to defect 1 than to defect 2 leads to $\Gamma_{1A} > \Gamma_{2A}$. Then the formation energy of defect 1 decreases faster than 2 for an increasing chemical potential of A. Although the initial

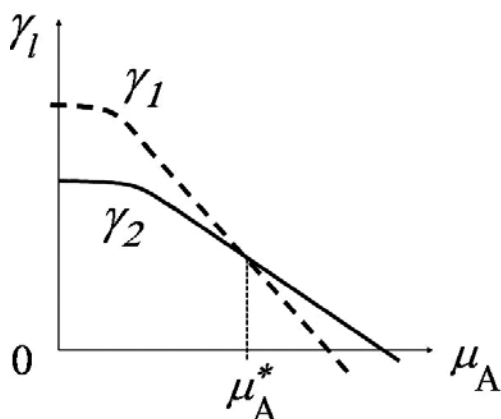


Fig. 3. Two defects of energy γ_1 and γ_2 are competing for defectant A. Despite a higher initial energy defect 1 will get a lower γ -value than defect 2 above a critical chemical potential of the defectant A μ_A^* , if the excess A (slope of the straight lines) is larger at defect 1 in comparison with defect 2. Then the generation of defect 1 on the expense of defect 2 becomes possible. This general treatment was used by Shewmon to describe void formation at grain boundaries [16].

formation energy of defect 1 (at zero concentration of A) may have been larger it may become smaller at higher values of μ_A . A graphic presentation of this behaviour is given in Fig. 3.

This behaviour has been used by Shewmon [16] to interpret void formation at grain boundaries during or before grain boundary fracture. In his study [16] he used a figure similar to Fig. 3 and states, "In each case, there is an impurity that adsorbs at the new (fracture) surface being formed. For the case of Fe–P alloys, a quantitative argument can show that adsorption of phosphorous on the free surface greatly reduces the barrier to void nucleation compared to that in the absence of phosphorous." In the terminology of this study phosphorous is the defectant, defect 1 is the surface (of the voids) and defect 2 is a grain boundary. During fracture under tensile load the imposed hydrostatic stress enhances void formation. This is not the case for void formation at grain boundaries of copper in the presence of bismuth.

Bismuth is known to segregate strongly at grain boundaries in copper [17]. The chemical potential μ_{Bi} can be increased by either increasing Bi-concentration or by rapid quenching from high to low temperatures where precipitation of Bi is suppressed and Bi-atoms are left in a highly supersaturated state. At values of μ_{Bi} being larger than the critical value μ_A^* shown in Fig. 3 other defects will be formed. This could be surfaces of voids at grain boundaries observed experimentally [18, 19] and generated without external stresses. This might also induce a transformation of one type of grain boundary (defect 1) into another faceted type (defect 2). Faceting of grain boundaries in copper with increasing Bi-content has also been observed experimentally [20]. For the case of void formation at grain boundaries the necessary condition of $\Gamma_{1A} > \Gamma_{2A}$ has been proven directly [21]. In the corresponding experiment voids were artificially produced in a copper bicrystal by welding two single-crystals containing grooves on their surfaces. After equilibrating with bismuth the sample was quenched. By intercrystalline fracture in UHV both the surface of the voids and the grain boundary area are exposed. Subsequent Auger-analysis revealed that the void surfaces had a much higher Bi-coverage than the adjacent grain boundary.

The author is grateful for receiving financial support from the Deutsche Forschungsgemeinschaft.

References

- [1] J.W. Gibbs: Trans Conn Acad, 1876, vol. III, 108–248 and 1878, vol. III, 343. Also in "The collected work of J.W. Gibbs", Vol. I, Longmans, Green and Co., New York 1928, p. 55.
- [2] J.W. Cahn, in: W.C. Johnson, J.M. Blakely (Eds.), Interfacial Segregation, ASM International, International Materials Park, OH 44073-0002, 1979, p. 3–23.
- [3] C. Wagner: Nachrichten der Akademie der Wissenschaften in Göttingen, II. Mathematisch-Physikalische Klasse 3 (1973) 1.
- [4] R. Kirchheim: Acta Mater. 55 (2007) 5129.
- [5] R. Kirchheim: Acta Mater. 55 (2007) 5139.
- [6] B.A. Hills: J. Appl. Physiol. 87 (1999) 1567.
- [7] H. Leita, A.M. Somoza, M.M. Telo da Gama: J. Chem. Phys. 105 (1996) 2875.
- [8] R.M. Pashley, M.E. Karaman: Applied Colloid and Surface Chemistry, Wiley, Ltd. New York (2004) p. 52.
- [9] R. Kirchheim: Acta Mater. 50 (2002) 413.
- [10] S.O. Nielsen, C.F. Lopez, P.B. Moore, J.C. Shelley, M.L. Klein: J. Phys. Chem. B 107 (2003) 13911.
- [11] I am grateful to Haili Wang from the Institute of Metals Research, Chinese Academy of Science, Shenyang, China for pointing my attention to this error.
- [12] Z. Łodziana, N.-Y. Topsøe, J.K. Nørskov: Nature Materials 3 (2004) 289.
- [13] Y. Fukai: Physica Scripta T 103 (2003) 11.
- [14] R.C. Reed RC: The superalloys: fundamentals and applications, Cambridge University Press (2006).
- [15] T.M. Pollock, R.D. Field: Dislocations and high temperature plastic deformation of superalloy single crystals. Dislocations in solids, vol. 11. Amsterdam: Elsevier (2002).
- [16] P.G. Shewmon: Metall. Mater. Trans. A 29 (1998) 1535.
- [17] E.D. Hondros, D. McLean: Phil. Mag. 29 (1974) 771.
- [18] D. Chatain, P. Wynblatt, G.S. Rohrer: Acta Mater. 53 (2005) 4057.
- [19] G. Wolde-Georgis, T. Al-Kassab: unpublished results.
- [20] U. Albert, H. Müllejan, M. Rühle: Acta Mater. 47 (1999) 4047.
- [21] G.A. Lopez, W. Gust, E.J. Mittemeijer: Scripta Mater. 49 (2003) 747.

(Received September 10, 2008; accepted December 14, 2008)

Bibliography

DOI 10.3139/146.110065
Int. J. Mat. Res. (formerly Z. Metallkd.)
100 (2009) 4; page 483–487
© Carl Hanser Verlag GmbH & Co. KG
ISSN 1862-5282

Correspondence address

Prof. Dr. Reiner Kirchheim
Institut für Materialphysik
Georg-August-Universität Göttingen
D-37077 Göttingen, Germany
Tel.: +49 551 39 50 02
Fax: +49 551 39 50 00
E-mail: rkirch@ump.gwdg.de

You will find the article and additional material by entering the document number **MK110065** on our website at www.ijmr.de