A time-resolved X-ray powder diffraction method to trace the decomposition of PdB_y solid solutions

T. G. Berger¹, A. Leineweber^{1,*}, E. J. Mittemeijer¹,
M. Knapp²

¹Max Planck Institute for Metals Research, Heisenbergstr. 3, D-70569 Stuttgart, Germany.

²Institute for Materials Science, Darmstadt University of Technology, Petersenstr. 23, D-64287 Darmstadt, Germany.

*Contact author; e-mail: a.leineweber@mf.mpg.de

Keywords: palladium-boron alloys, miscibility gap, compositional changes, line broadening

Abstract. A powder diffraction method is presented for reconstructing probability density functions for the composition, $p(y)$, of a PdB_y solid solution material with composition (y)-dependent lattice parameter from the simultaneous analysis of all reflections in the powder diffraction patterns. The method is applied to the decomposition of a solid solution in a miscibility gap: two ‘boundary phases’ appear which gradually approach but don’t attain fully the compositions of the expected equilibrium phases whereas a significant amount of material with intermediate compositions remains.

Introduction

X-ray powder diffraction provides information about the atomic structure (size and symmetry of unit cell, atom positions and displacements) of crystalline materials via the positions (Bragg angles) and intensities of reflections. Analysis of the width and shape of diffraction-line profiles, furthermore, allows extraction of microstructural information, e.g. in terms of microstrain and crystallite size [1]. Analysis of this *physical broadening*, denoted f , is, however, considerably hindered by the instrumental contribution g , with which f is convoluted leading to the real measured profile h . Various convolution and deconvolution methods exist to determine the physical from the measured profile [2]. The present work aims at developing a method to reconstruct complicated *probability density functions* for composition, $p(y)$, of a solid solution material, with composition (y)-dependent lattice parameters, from the simultaneous analysis of *all* reflections in the powder pattern.

The solid solution considered here is the palladium-rich solid solution PdB_y . It exhibits an extraordinarily high interstitial solid solubility up to about $\text{PdB}_{-0.25}$ above temperatures of 440°C (y in PdB_y denotes both the atomic ratio and the occupancy by boron atoms of the octahedral sites in the *ccp* palladium host lattice) as well as several low-temperature phases and two-phase fields below temperatures of about 400-450°C [3]. A remarkable and for binary interstitial solid solutions rare feature is the miscibility gap with a critical temperature

of $T_{\text{crit}} = 410^\circ\text{C}$ which covers at the monotectic temperature of $T_{\text{mono}} = 312^\circ\text{C}$ a composition range of about $0.03 < y < 0.10$ (figure 1) [4, 5]. Decomposition in this miscibility gap upon annealing can be considered as a redistribution of boron atoms over the octahedral interstices leading to changes in the probability density function for composition $p(y)$ as averaged over the sample, which shows up in a characteristic way in powder diffraction patterns.

Figure 1. Part of the Pd-B phase diagram with the miscibility gap [3]. The grey shaded area shows the phase field of the solid solution.

Figure 2. 311-Diffraction peak group ($\text{CuK}\alpha_1$ radiation) recorded from a $\text{PdB}_{0.064}$ sample annealed for various times at 340°C .

Experimental

Preparation and heat treatment

$\text{PdB}_{0.064}$ was prepared by arc melting under argon from weighted amounts of palladium foils and an appropriate amount of boron pieces. $\text{PdB}_{0.050}$, previously used in a neutron diffraction study, was prepared similarly from ^{11}B [7]. Both reguli were checked for homogeneity [5-7]. The powder samples (filed from the reguli) were sealed under vacuum in quartz capsules, annealed at 800°C for 5 min and subsequently quenched in water. The annealing was performed to relieve deformation stresses due to the filing procedure. The composition was calculated [6] by

$$a = a_0 + \alpha \cdot y = 3.8920 + 0.6882y \text{ [Å]} \quad (1)$$

The heat treatments for the decomposition were performed from 3 hours till up to 8 weeks (in sealed quartz tubes encapsulated in a salt bath for up to 4 days, longer annealings in a furnace) at 340°C or 355°C with subsequent water quenching.

X-ray diffraction measurements

X-ray powder diffraction measurements of the initial, stress-relieved solid solution and of the subsequently annealed samples were performed

- *in house* on a Philips X'Pert MPD instrument ($\text{CuK}\alpha_1$ radiation in Bragg-Brentano geometry, powder samples were deposited as a thin layer together with internal silicon standard powder on Si wafers cut parallel to the (510) plane) and
- for two selected $\text{PdB}_{0.064}$ specimen, one quenched from 800°C to preserve the solid solution and one annealed for 18 days at 340°C to evoke the decomposed state, employing synchrotron radiation with $\lambda = 1.1315 \text{ Å}$ on the B2 beamline [8], HASYLAB, Hamburg (no internal standard, separate LaB_6 standard (SRM 660a) measurements; powder deposited on Kapton foil, measurements performed in transmission geometry).

All reflections were recorded by measuring over 2θ (diffraction-angle) subranges sufficiently large to determine the background at both sides of each reflection (group).

Data evaluation method

The decomposition of the initially homogeneous solid solution into a boron-rich and a boron-poor solid solution phase is clearly revealed by the occurring splitting of the Bragg reflections. For short annealing times (e.g. figure 2), the original solid solution is still present. Even after the longest applied heat-treatment times (8 weeks at 340°C and 2 weeks at 355°C), still considerable diffraction-line broadening remains which is asymmetric for both the high and the low boron components ('boundary phases') such that residual intensity between the pairs of reflections remains. To analyse the time-dependent decomposition as observed in the X-ray diffraction patterns, the reflection profiles were modelled using the program TOPAS [9] as described below.

X-ray data evaluation

For each heat treatment, all individually measured reflections, from PdB_y as well as from the internal standard (*in house* data), were merged into one data set after manually subtracting the background. This complete pattern was modelled in a Rietveld-like fashion, considering a convolution of three line-broadening contributions:

$$h = g \otimes f_1 \otimes f_2 \quad (2)$$

with g and f_1 taken as *Voigt* functions with angle-dependent Gaussian and Lorentzian full width at half maximum values B_L and B_G , respectively. The instrumental profile g was determined from the internal Si standard (*in house* data) or the separately measured LaB_6 standard (*synchrotron* data), respectively, by fitting LY , LX , GU , GV , GW according to:

$$g: \quad B_{g,L} = LY \tan \theta + LX / \cos \theta; \quad B_{g,G}^2 = GU \tan^2 \theta + GV \tan \theta + GW. \quad (3)$$

The structural line broadening f_1 of the two quenched solid solution samples was described semi-empirically by size and anisotropic microstrain broadening, fitting L_1 , L_2 , S_1 , S_2 , G_2 :

$$f_1: \quad B_{f_1,L} = L_1 \tan \theta + L_2 / \cos \theta; \\ B_{f_1,G}^2 = \left(S_1 + S_2 \frac{h^2 k^2 + k^2 l^2 + h^2 l^2}{(h^2 + k^2 + l^2)^2} \right) \tan^2 \theta + (G_2 / \cos \theta)^2. \quad (4)$$

The present description of the microstrain broadening anisotropy was derived from the assumption of an isotropic microstress distribution leading to anisotropic microstrain if the crystals are elastically anisotropic [10] (as is the case for Pd).

The additional line broadening occurring in the diffraction patterns of the annealed specimen, f_2 , can be attributed to the occurrence of decomposition-induced compositional variations described by $p(y)$, starting from a delta-shaped distribution for the initial solid solution. For the annealed samples $p(y)$ was approximated by a frequency polygon (figure 3) with composition steps of $\Delta y = 0.001$. Due to the composition dependence of the lattice parameters of the cubic crystal lattice (equation (1)) of PdB_y , $p(y)$ reflects itself directly in each reflection [11]. In Topas [9] this was incorporated in terms of a multiphase refinement of 120 'phases' with composition values y' which are spaced by Δy . Each 'phase' $\text{PdB}_{y'}$ has been ascribed a compositional line broadening contribution corresponding to a trapezoid (shaded in grey in figure 3) with a width of $2\alpha\Delta y \tan \theta a$ (cf. equation (1)), and an area (integral intensity) proportional to $(p(y') + p(y' + \Delta y))/2$.

Penalty functions to achieve stability in refinements of $p(y)$

Refining the $p(y')$ values without any constraints leads to severe correlations between different $p(y')$ [12,13]. These correlations can be reduced to achieve physically realistic 'smooth' $p(y)$ by application of so-called penalty functions (PF). These serve as contribution to the overall χ_{pen}^2 (*penalised least squares*), additional to the usual χ^2 from the difference between observed and the calculated profile [14]:

$$\chi_{pen}^2 = \chi^2 + (K \cdot PF)^2 \quad K: \quad \text{penalty weighting factor [9]} \quad (5)$$

Commonly [12,13], these penalty functions are modified integrals of the first or second derivatives of $p(y)$, e.g. as used here:

$$PF_1 = \int q_1 \cdot (p'(y))^2 dy \quad q_1: \quad p^{-1}(y). \quad (6)$$

$$PF_2 = \int q_2 \cdot (p''(y))^2 dy \quad q_2: \quad (C^2 + (p''(y))^2)^{-1}. \quad (7)$$

A compromise for the weight K of the penalty function contribution to the overall χ^2 must be found to obtain a reasonable $p(y)$: In case of too low weight the correlations are not sufficiently suppressed; in case of a too high weight, physical features in the shape of $p(y)$ may be suppressed ('*oversmoothing*') [13]. In the present case, the application of the penalty function was allowed to increase the χ^2 value by not more than 10% as compared to the value obtained with an unconstrained refinement. For most of the performed refinements, PF_1 produced satisfactory results; PF_2 (with another constant C to be adjusted empirically) was only used for the refinement of the microstrain broadening (see Results).

Figure 3. Frequency polygon type description of the probability density function of composition $p(y)$ and the corresponding line-broadening f_2 for the 311-reflection. The grey area shows the contribution associated with composition $y=0.061$ (with an area proportional to $(p(y') + p(y' + \Delta y))/2$).

Results and Discussion

Results for $p(y)$ obtained with the described method are shown in figures 4a-c for $\text{PdB}_{0.064}$ and $\text{PdB}_{0.050}$ annealed for various times at 340°C and $\text{PdB}_{0.050}$ annealed for various times at 355°C.

Initially, $p(y)$ contains a remaining contribution from the original solid solution. Its phase fraction was determined by subtracting an estimated parabolic 'background $p(y)$ ' between the two 'boundary phases' (figure 4a). The time-dependence of the molar phase fraction (referring to the formula PdB_y) of the parent solid solution is similar for the three samples, but the $\text{PdB}_{0.064}$ sample decomposes much faster than the $\text{PdB}_{0.050}$ at the same temperature of 340°C. Further, $\text{PdB}_{0.050}$ decomposes faster at 340°C than at 355°C (figure 5). Therefore the driving force for the decomposition has its maximum in the middle of the miscibility gap.

The values of the boundary (product) phase compositions (figure 6) were determined by a parabolic fit to the three locally highest $p(y')$ values in the range of the local maxima pertaining to the high and low boron product phases. For short annealing times the $p(y)$ of the $\text{PdB}_{0.050}$ sample, annealed at 355 °C, did not show clear local maxima for the ‘boundary phases’, therefore the two shortest annealing times were omitted. For long annealing times, differences in the ‘boundary phase’ composition for the same temperature occur, which are not expected by the phase diagram (cf. figure 6).

Figure 4a-c. $p(y)$ for different annealing times and different initial compositions. Clearly visible is the faster decomposition for $\text{PdB}_{0.064}$ compared to $\text{PdB}_{0.050}$ and for 340°C compared to 355°C (estimation of the fraction of initial solid solution has been indicated in 4a).

Figure 5. Relative phase fractions of the initial solid solutions vs. annealing time.

Figure 6. Boundary product phase compositions vs. annealing time. For $\text{PdB}_{0.050}$ at 355°C the shorter annealing times could not be analysed (see text).

So far in the analysis the line profile parameters of the microstructural line-broadening, f_1 , were kept constant and taken equal to those determined for the initial solid solution. Since the mechanical microstrain broadening is anisotropic (cf. equation (4)), it should be possible to detect a change in f_1 upon decomposition, given sufficient resolution of the data, as it was the case for the *synchrotron* measurements. Unconstrained refinement of S_1 and S_2 (equation (4)) was not possible due to the correlation of the S_1 parameter with the also $\tan\theta$ -dependent line broadening due to $p(y)$. Therefore the ratio S_1/S_2 was fixed to the value of the initial solid solution. By stepwise increasing S_1 and S_2 it could be shown that there is indeed an increase of microstrain broadening upon decomposition. The first derivative as used in PF_1 has its highest values at the inflection points of $p(y)$ located at the ‘flanks’ of $p(y)$, thus the penalty function may suppress subtle width-related effects. Therefore, for the analysis of S_1 and S_2 , the penalty function PF_2 was employed which has its highest values at the maxima of $p(y)$. The resulting $p(y)$ are shown in figure 7 for the initial solid solution values of S_1 and S_2 characterising the anisotropic microstrain broadening and for 5 S_1 and 5 S_2 ; in the last case a distinctly improved fit to the measured diffraction pattern was achieved. It follows that

changes in S_1 and S_2 influence $p(y)$: broader f_1 due to higher values of S_1 and S_2 leads to a 'sharpened' $p(y)$ (figure 7).

Figure 7. $p(y)$ as determined from synchrotron data adopting microstrain broadening parameters S_1 and S_2 equal to those of the solid solution (left) and 5 times as large (right) (PF_2 applied).

Conclusions

A method has been presented to determine presuppositionlessly composition distributions of decomposing solid solutions from complicated diffraction-line profile shapes in an simultaneous evaluation of all reflections in a powder diffraction pattern. This composition distribution is determined by convolution fitting of a probability density function $p(y)$ with an instrumental broadening contribution g measured by internal standards and a microstrain and size broadening contribution f_1 measured from a parent solid solution sample.

References

1. Delhez, R., de Keijser, Th. H., Mittemeijer, E. J., 1982, *Fresenius Z. Anal. Chem.* **312** (1), 1.
2. Snyder, R. L. & Fiala, J. & Bunge, H.-J., 1999, *Defect and Microstructure Analysis by Diffraction* (Oxford University Press), chapter 26 -27.
3. Liao, P. K., Spear, K. E., Schlesinger, M. E., 1996, *J. Phase Equilib.* **17**, 340.
4. Alqasmi, R. A., Brodowsky, H., Schaller, H.-J., 1982, *Z. Metallkde.* **73**, 331.
5. Beck, M., Mittemeijer, E. J., 2001, *Z. Metallkde.* **92**, 1271.
6. Beck, M., Ellner, M., Mittemeijer, E. J., 2001, *Acta Mater.* **49**, 985.
7. Berger, T. G., Leineweber, A., Mittemeijer, E. J., Fischer, P., 2004, *Phys. Stat Sol. A* **201**, 1484.
8. Knapp, M., Baecht, C., Ehrenberg, H., Fuess, H., 2004, *J. Synchrotron Rad.* **11**, 328.
9. TOPAS, *General Profile and Structure Analysis Software for Powder Diffraction Data*, V2.0, Bruker AXS GmbH, Karlsruhe, Germany.
10. Stokes, A. R., Wilson, A. J. C., 1944, *Proc. Phys. Soc.* **56**, 174.
11. Leineweber, A., Mittemeijer, E. J., 2004, *J. Appl. Cryst.* **37**, 123.
12. Good, I. J., Gaskins, R. A., 1971, *Biometrika* **58**, 255.
13. Louboutin, R., Louër, D., 1969, *Acta Cryst. A* **25**, 335.
14. Coelho, A. A., 2000, *J. Appl. Cryst.* **33**, 899.