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Thermodynamics of hydrogen solution and hydride formation for different microstructures of Pd

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Abstract

Relative partial enthalpies, ΔH_{H} for H_2 solution in Pd have been measured by reaction calorimetry for annealed (1373 K), cold-worked, cycled through the hydride phase change and the combination of (cycled+cold-worked) forms. The partial enthalpies for H_2 solution in Pd as H/Pd→0 increase in exothermicity in the order: annealed, cold-worked, (cycled+annealed) and (cycled+cold-worked) Pd. The ΔH_{H} values in the dilute phase undergo a nearly discontinuous transition to ΔH_{plat} for annealed Pd but they gradually increase to the plateau values for cycled Pd paralleling the trends in the isotherms.

Keywords: Palladium microstructures; Hydride formation; Partial enthalpies

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1. Introduction

There have been many measurements of H_2 isotherms for the Pd–H system with substantial agreement for annealed Pd. There are fewer isotherms available for different microstructures of bulk Pd, i.e. cold-worked, hydrided/dehydrided (cycled) but there are no detailed studies of the dilute phase solubility using calorimetry. The most recent calorimetric study did not report any detailed dilute phase data [1].

It is known that Pd containing large dislocation densities from cold work or from cycling, or from their combination, has H_2 solubility in the dilute phase enhanced compared to the annealed form due to the attraction of H atoms to dislocation stress fields [2,3]. Dislocations are more uniformly distributed after cycling Pd as compared to cold-working where they are primarily in cell walls [4]. This may help to explain the observation that the solubility increments are additive for cold-worked and cycled Pd [5], i.e. for the solubility increments: Pd (cycled+cold-worked)=Pd (cold-worked)+Pd (cycled) where the solubility increment is the increase in r relative to annealed Pd at a given p_{H_2} and (cycled+cold-worked) indicates that the sample was first cold-worked and then cycled.

Pressure–composition–temperature, p–c–T, data are well-suited for obtaining precise thermodynamic data for the dilute phase of annealed Pd [6,7], however, this approach is not the most appropriate one for obtaining such data for Pd containing high dislocation densities because the distribution of H between the dislocation stress fields and normal interstices is temperature dependent and the van't Hoff-type plots will be affected by this redistribution. On the other hand, in quasi-isothermal calorimetric measurements the enthalpies reflect only the dislocation stress field–H interactions at the temperature of the calorimetry.

Although there is good agreement for the thermodynamic parameters of the dilute phase of Pd (annealed)–H derived from p–c–T data [6–8], it is desirable to determine ΔH_{H} values by calorimetry for comparison with the results to be obtained for high dislocation density Pd.

Hysteresis affects ΔH_{H} values obtained from p–c–T data in the plateau region whereas calorimetric data are unaffected [9] and therefore the latter method is preferred. Because of the sharp rise in p_{H_2} with r in the hydride single phase, the p_{H_2} values are markedly affected by small changes of r=H/Pd and, consequently, small errors in r at different temperatures lead to large errors in the thermodynamic parameters. Reaction calorimetry is therefore also the preferred method for obtaining thermodynamic parameters for this region.

There is evidence for the trapping of H in vacancies generated by cold-work or by cycling of Pd [10,11]. One motive for this research is to characterize this trapping by calorimetry. The main motive of the research is, however, to determine how different microstructures of bulk Pd

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affect its H_2 solubility and the corresponding thermodynamic parameters.

2. Experimental

The calorimeter employed has been described elsewhere [1]. The samples (≈1.6 g) were prepared by cutting Pd foil (≈100 μ thickness) into small pieces and mixing with about twice as much Cu powder (by weight) before insertion into the calorimeter vessel. The Cu serves as a heat transfer material which does not absorb hydrogen. All measurements were made at 303 K. The errors in the calorimetric values depend on heat magnitudes and on the moles of H absorbed or desorbed, i.e. $\Delta H_H = (\delta q/\delta n_H)$. The error is greatest in the single phase regions and especially in the very dilute region, where the heats are small and in the high H content region where the δn_H values are more uncertain. In the dilute phase the error in ΔH_H due to the heat measurement is ±0.5 kJ/mol $1/2H_2$ where other possible errors are difficult to evaluate, e.g. small baseline shifts in the calorimeter output.

Pd was cold-worked by rolling foils to approximately half of their initial thickness by a series of rollings with each roll perpendicular to the previous one, cross-rolling. The foils were then cut into small pieces. Ross et al. [12] have argued that this procedure produces a more stable dislocation network than unidirectional rolling where, according to them, the introduction of H eliminates some dislocations. These Pd samples will be referred to as cold-worked with the understanding that they have been cross-rolled as described.

Pd annealed at 1373 K is large grained; many grains extend across the whole sample thickness. The grains become smaller after cycling. TEM has been used here and elsewhere for the examination of Pd which has been cycled and there are very large dislocation densities.

3. Dilute phase H_2 isotherms and enthalpies for Pd of various microstructures determined by reaction calorimetry

Fig. 1 shows dilute phase H_2 isotherms (303 K) for annealed (1373 K) Pd along with $|\Delta H_H|$ values. The $p_{H_2}^{1/2}$ – r (=H/Pd) data for the annealed form (1373 K) agrees quite well with data from Wicke and Nernst [6]. There is a supersaturation of the dilute phase shown by greater p_{H_2} values near the transition than at higher r; this is seen more clearly on the complete isotherm (see below).

There is some scatter in the $|\Delta H_H|$ results (303 K) because of the small increments of H employed (Fig. 1). From p–c–T data for annealed Pd, $|\Delta H_H| = 10.2$ kJ/mol $1/2H_2$ as $r \rightarrow 0$ and, because of the H–H attractive interaction energy, it increases by 0.6 kJ/mol $1/2H_2$ from $r = 0$ to 0.016 [6,7]. At the (dilute/(dilute+hydride)) phase boundary there should be a discontinuous change of $|\Delta H_H|$ from the dilute phase value of 10.8 kJ/mol $1/2H_2$ to the plateau value of 19.2 kJ/mol $1/2H_2$ [1,6,7] but, in the present data, there are some intermediate values (Fig. 1). For Pd (annealed, 1373 K) in the dilute range from $r = 0$ to about 0.010, $|\Delta H_H|$ is about 10 kJ/mol $1/2H_2$ and for $r = 0.010$–0.020 some enthalpy values are 12 kJ/mol $1/2H_2$ and others closer to the plateau value, i.e. 17.2 and 18.9 kJ/mol $1/2H_2$ (Fig. 1). By comparison with the isotherm (Fig. 1) the values of $|\Delta H_H|$ which fall near 12 kJ/mol $1/2H_2$ are clearly in the dilute phase and this difference from the expected value of 10.8 kJ/mol $1/2H_2$ must be experimental error.

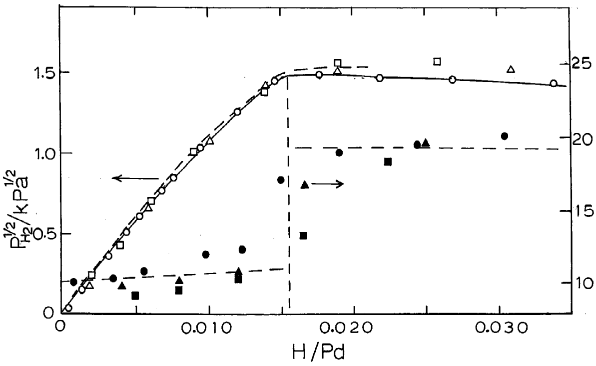

Fig. 1. Dilute phase H_2 isotherms and $|\Delta H_H|$ values for annealed (1373 K) Pd at 303 K. The different symbols are for different sets of determinations and the open and filled symbols are for the isotherms and $|\Delta H_H|$, respectively, as indicated by the arrows.

Values of $|\Delta H_H|$ in the range ≈17 kJ/mol $1/2H_2$ correspond to the contents where supersaturation in the isotherm occurs suggesting that supersaturation arises from coherent rather than incoherent nucleation of the hydride phase since the former would be expected to have a lower $|\Delta H|$ than the incoherent, plateau value. When the nuclei grow and become incoherent, $|\Delta H|$ increases to the normal plateau value, $|\Delta H_{plat}|$. It is known that coherent nucleation takes place initially in β phase Pd–H and that there is then a conversion to incoherency [13]. Thus supersaturation is likely to be due to the coherent→incoherent transition and not to a lack of nucleation of the hydride phase.

Another possible explanation for these $|\Delta H_H|$ values of ≈17 kJ/mol $1/2H_2$ is that some hydride formation may take place below the formation plateau pressure, p_f, as shown earlier [14], i.e. it can occur under conditions where: $p_{dosing} \gg p_f$ and $p_{final} > p_d$ and where the H diffusion constant is small; p_d is the decomposition plateau pressure. Thus hydride phase forms near the surface layers due to slow diffusion, and even when H leaves this hydride phase as it does during a desorption hysteresis scan [15] the hydride phase cannot decompose unless $p_{final} \leq p_d$. These conditions are most likely to be fulfilled at low

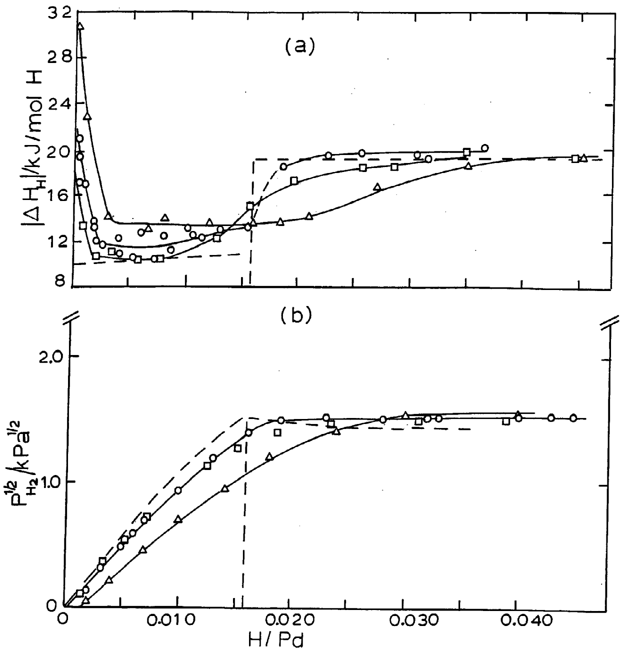

Fig. 2. (a) Dilute phase $|\Delta H_H|$ values and (b) H_2 isotherms for different microstructures of Pd: ○, cold-worked; □, cycled annealed (1373 K); △, cycled cold-worked.

temperatures and such hydride formation was observed at 233 and 243 K [14]. Hydride formation by this mechanism seems unlikely in the present experiments because of the higher temperature and because p_{dosing} is not so much greater than p_f and because there is no indication of any hydride formation from the dilute phase isotherm. Therefore the intermediate $|\Delta H|$ values are most likely due to coherent nucleation. Although a discontinuous change in $|\Delta H|$ values is not seen (Fig. 1), the intermediate values can be rationalized as due to some experimental error, or to coherent nucleation.

Results for Pd containing large dislocation densities are shown in Fig. 2a and b where (a) shows the partial enthalpies and (b) shows the dilute phase isotherms. The (dilute/(dilute+hydride)) phase boundary for annealed Pd–H is indicated by the vertical line at $r = 0.016$ (303 K).

A solubility enhancement, $(r'/r)p_{H_2}$, can be defined where r' and r are the H/Pd ratios for Pd with large dislocation densities and for annealed Pd, respectively, at a given p_{H_2}. Solubility enhancements can be evaluated from the isotherms (Fig. 2b) and are shown in Table 1. After cycling cold-worked Pd, its solubility enhancement increases from $(r'/r)_{1.2\ \text{kPa}} = 1.22$–$1.44$. After cycling annealed Pd (1373 K) its solubility enhancement is 1.23 (303 K).

Results for 'flame annealed' Pd are also shown in Table 1. 'Flame annealing' consists of heating Pd to a bright red heat in an oxygen/gas torch for a few moments and then quickly cooling in air. Pd oxide is unstable above about 1100 K and will not reform if the Pd is cooled quickly. Although this annealing appears to be crude, it is, nonetheless, an effective method for rapid annealing and is found to produce similar H_2 isotherms as Pd annealed in vacuo at, e.g. 1073 K. The solubility enhancement is greater for Pd which was annealed by flaming than by the higher temperature annealing (1373 K) where the grains are larger.

There is an initial region where p_{H_2} is very small for cold-worked Pd leading to a finite intercept along the r-axis and there is a similar, but greater, intercept after cycling it (Fig. 2b). The intercept for the cold-worked Pd is similar to that observed before for cold-worked Pd at 273 K [10]. This region is suggested to be due to the occupation of vacancies by H.

The transition to the plateau p_{H_2} is more gradual for cycled (Fig. 2b) than for annealed Pd where there is a supersaturation in the dilute phase isotherms. The dilute H_2 solubility for cycled, annealed (1373 K) Pd is of interest because the solubility enhancement is initially small and then increases slowly and continuously to the plateau. Its solubility differs from the (cycled+cold-worked) sample which has a large solubility enhancement over the whole dilute solubility range (Fig. 2b).

Fig. 2a shows the $|\Delta H_H|$ values for Pd containing large dislocation densities. The enthalpy values for cold-worked Pd are greater, ≈18 kJ/mol H as $r \rightarrow 0$ than for annealed Pd, 10.2 kJ/mol H. For H contents between about $r = 0.003$ and 0.015, the $|\Delta H_H|$ values are about 12 kJ/mol H rather than 10.6 kJ/mol H for annealed Pd obtained from p–c–T data [6,7] or as found here approximately from calorimetry (Fig. 1). There is a relatively abrupt transition to the plateau values at about $r = 0.016$ shown by the dashed line which is reminiscent of annealed Pd (Fig. 1). This is consistent with the isotherm which, despite the solubility enhancement, approaches the plateau more sharply than cycled Pd (Fig. 2a).

Further dislocations are introduced by cycling cold-worked Pd, and the two methods of dislocation introduction lead to dislocation densities which are additive

Table 1
Solubility enhancements for Pd–H (303 K, 1.2 kPa)

Annealed	Cold-worked	Cycled + cold-worked	Cycled + annealed	Cycled + flame annealed
1.00	1.22	1.44	1.23	1.46

according to the solubility increments (which is apparent after shifting the solubility results to intersect the origin, Fig. 2b, or from Ref. [5]). Fig. 2a shows that the $|\Delta H_H|$ values are greatest after cycling cold-worked Pd and for this microstructure there is a continuous increase of $|\Delta H_H|$ to the plateau value over the range from $r \approx 0.02$–0.03.

For the most heavily dislocated Pd, (cycled + cold-worked), $|\Delta H_H|$ is ≈30 kJ/mol 1/2H$_2$ as $r \rightarrow 0$ (Fig. 2a). The reported experimental value of $|\Delta H_H|$ for the occupation of vacancies in Pd is 32 kJ/mol 1/2H$_2$ from the thermal desorption of ion implanted H [16] and the theoretical value is 25 kJ/mol 1/2H$_2$ [17]. A much larger Pd sample would be needed for the present calorimeter than that employed here in order to obtain a reliable enthalpy for the occupation of vacancies by H but, nonetheless, the observed enthalpies are of the correct order of magnitude (Fig. 2a) and suggest that vacancy trapping of H occurs.

The increased values of $|\Delta H_H|$ relative to annealed Pd observed from about $r = 0.002$ to 0.015 for cold worked or cycled Pd are due to H segregation into the tensile stress fields of edge dislocations. H simultaneously occupies both the stressed and normal octahedral interstices, and since the measured $|\Delta H_H|$ values reflect occupation of both, the enthalpies for segregation of H to the stress fields cannot be obtained without knowing the fraction of each type. Because of the greater trapping energy, all of the H atoms occupy vacancies at very low r.

The $|\Delta H_H|$ values from about $r = 0.015$ to the plateau increase steadily for (cycled + annealed) or (cycled + cold-worked) Pd (Fig. 2a) differing from both the annealed and cold-worked Pd where, despite the fact that there are several enthalpies shown in the transition region (Figs. 1 and 2a), the transitions to the plateau, nonetheless, appear to be relatively sharp. By contrast with annealed Pd, for cycled Pd there is evidence available in the literature [15], e.g. irreversibility in the dilute phase solubility, suggesting that the steady increase of $|\Delta H_H|$ to the plateau can be attributed to limited amounts of hydride formation in favored regions.

The shapes of the dilute phase isotherms and the corresponding $|\Delta H_H|$ values (Fig. 2) for (cycled + annealed (1373 K)) Pd are of interest because the latter values are smaller than those for the uncycled, cold-worked Pd, however, by contrast with the latter, they increase continuously as the plateau is approached reflecting the isotherm which also slowly approaches the plateau (Fig. 2). Thus cycling produces extended defects in Pd where hydride formation can occur below the normal plateau p_{H_2}. Dissolved H has been used as a probe for defects in Pd and its alloys [3] and it seems that an extended defect introduced by cycling, but not by the cold-rolling employed here has been detected via H$_2$ solubility. Such an ‘extended defect’ may be relatively large regions of internal stress introduced by cycling which would allow hydride formation at p_{H_2} below the plateau pressure in the tensile stressed regions. It is known that metals subjected to *cyclic* cold-working, which is analogous to hydrided cycling, develop long range internal stresses [18].

4. Complete isotherms and enthalpies (303 K) for Pd of different microstructures

Complete isotherms are shown in Fig. 3 for the four different microstructures. The initial absorption isotherm is quite horizontal for annealed (1373 K) Pd with a clear delineation of the (dilute + hydride)/hydride phase boundary where a sharp increase in p_{H_2} occurs. The second isotherm, i.e. one for the cycled Pd, is more sloping with a less-clear phase boundary. For cold-worked Pd the initial absorption isotherm is quite sloping and its plateau p_{H_2} is higher than that for the annealed (1373 K) Pd; its p_{H_2} plateau is higher for the second cycle than the first and, in contrast to annealed Pd, it is more horizontal. The desorption isotherm was measured for (cycled + cross-rolled) Pd and its p_{H_2} values are lower than those for annealed Pd. The end of the two-phase region where p_{H_2} commences to rise steeply is the same for all the microstructures.

The corresponding enthalpies are shown in Fig. 4; these can be compared to earlier values obtained by Flanagan et al. shown by the dashed line [1]. There is good agreement between the present results and the earlier ones with no discernable difference between $|\Delta H_{plat}|$ for absorption or desorption.

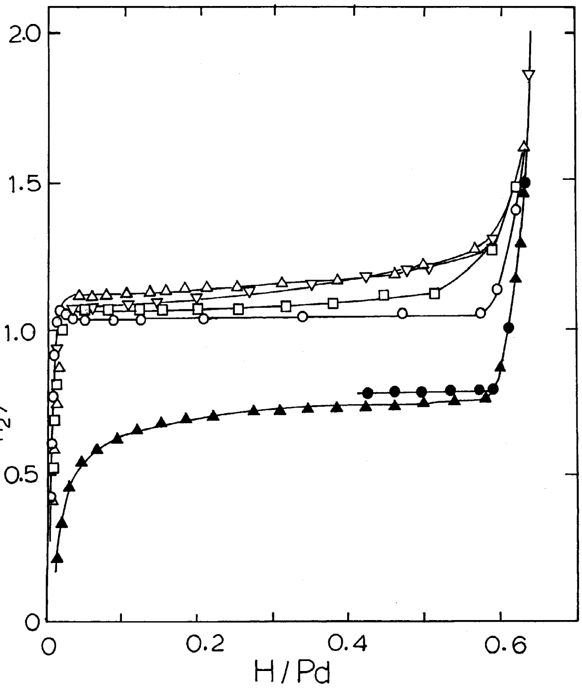

Fig. 3. Isotherms (303 K) for the various microstructures of Pd. ○, Annealed (1373 K); ▽, cold-worked; △, cycled cold-worked, and □, cycled annealed (1373 K). Open symbols are for absorption and filled ones for desorption.

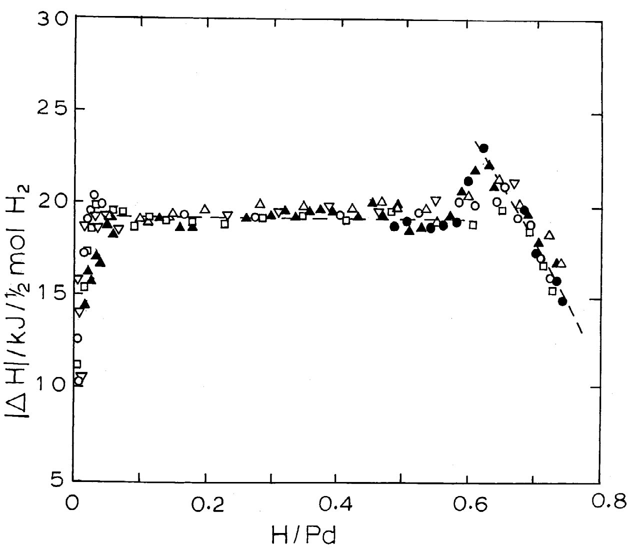

Fig. 4. Calorimetric $|\Delta H_H|$ and $|\Delta H_{plat}|$ values (303 K) for different microstructures of Pd. ○, Annealed (1373 K); ▽, cold-worked; △, cycled cold-worked, and □, cycled-annealed (1373 K). Open symbols are for absorption and filled ones for desorption.

There are no marked differences in the $|\Delta H|$–r plots for the various microstructures except for the dilute phase (Figs. 1 and 2). A small increase at the (dilute/(dilute+hydride)) phase boundary was observed for some samples during absorption but not during desorption; this was not observed in the earlier study [1] and may be an experimental artifact.

The behavior of $|\Delta H_{plat}|$ at the upper phase boundary and at higher r values has been reported earlier [1] and has been inferred from p–c–T data [6] (Fig. 4). Basically, there is an almost linear decrease in $|\Delta H_H|$ values with r from about $r=0.62$ to 0.74. During desorption the $|\Delta H_H|$ values are greater than for absorption at similar r values. This is a result of hysteresis, i.e. the hydride→dilute transition takes place at smaller r values than the dilute→hydride transition during absorption.

The relative partial entropy magnitudes from 0.62 to 0.70 are constant at 60±2 J/K mol $1/2H_2$ which can be calculated from the ideal equation $\Delta S_H = \Delta S_H{}^\circ - R\ \ln(r/(1-r))$ where $\Delta S_H{}^\circ = -54$ J/K mol $1/2H_2$. This is a reasonable approximation because the excess, non-ideal partial entropy is small in this region of r due to its change from negative to positive at about $r=0.64$ [8].

5. Conclusions

There are differences in the dilute phase H_2 solubilities and partial enthalpies, $|\Delta H_H|$ between 'defect-free', annealed Pd and Pd having microstructures characterized by high dislocation densities. Large negative enthalpies are found as $r \rightarrow 0$ for the latter compared with the annealed form. This reflects trapping in especially energetic sites believed to be Pd vacancies generated during the cycling or cold-working. $|\Delta H_H|$ values are also greater for the cold-worked form up to the normal dilute phase boundary and for cycled forms at contents greater than the dilute phase boundary for annealed Pd; there is a continuous increase up to the plateau at about $r=0.040$ for the (cycled+cold-worked) form. The isotherms parallel these results.

These results should be qualitatively applicable to other metal–H systems and to Pd-rich alloys, i.e. the $|\Delta H_H|$–r relations in the dilute phase will differ for annealed and cycled/cold-worked forms with the latter $|\Delta H_H|$ values being greater at H contents below the normal phase boundary and then slowly increasing well beyond the normal phase boundary to the plateau enthalpy.

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References

[1] T. Flanagan, W. Luo, J. Clewley, J. Less-Common Metals 172–174 (1991) 42.
[2] T. Flanagan, J. Lynch, J. Clewley, B. von Turkovich, J. Less-Common Metals 49 (1976) 13.
[3] R. Kirchheim, Prog. Mater. Sci. 32 (1988) 361.
[4] B. Heuser, J. King, J. Alloys Comp. 261 (1997) 225.
[5] J. Lynch, J. Clewley, T. Curran, T. Flanagan, J. Less-Common Metals 55 (1977) 153.
[6] E. Wicke, G. Nernst, Ber. Bunsenges Phys. Chem. 68 (1964) 224.
[7] T. Flanagan, W. Oates, Annu. Rev. Mater. Sci. 21 (1991) 269.
[8] T. Kuji, W. Oates, B. Bowerman, T. Flanagan, J. Phys. F: Met. Phys. 13 (1983) 1785.
[9] T. Flanagan, C.-N. Park, Mater. Sci. Forum 31 (1988) 297.
[10] T. Flanagan, S. Kishimoto, in: P. Jena, C. Satterthwaite (Eds.), Electronic Structure and Properties of Hydrogen in Metals, Plenum Press, New York, 1983.
[11] R. Kirchheim, Acta Metall. 34 (1986) 37.
[12] D. Ross, K. Stefanopoulos, M. Kemali, J. Alloys Comp. 293–295 (1999) 346.
[13] H. Jamieson, G. Weatherly, F. Manchester, J. Less-Common Metals 50 (1976) 85.
[14] T. Flanagan, T. Kuji, J. Less-Common Metals 99 (1984) L5.
[15] T. Flanagan, S. Kishimoto, G. Biehl, in: Chemical Metallurgy — A Tribute to Carl Wagner, The Metallurgical Society AIME, Warrendale, OH, 1981, p. 471.
[16] S. Myers, W. Wampler, F. Besenbacher, S. Robinson, Mater. Sci. Eng. 69 (1985) 397.
[17] S. Myers, P. Richards, W. Wampler, F. Besenbacher, J. Nucl. Mater. 165 (1992) 9.
[18] D. Kuhlmann-Wilsdorf, Metall. Trans. 16A (1985) 2091.