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Abstract

As metal-hydrogen (M-H) systems possess, among others, the capability of temporarily storing hydrogen (H), they are considered as a safe energy carrier of the future; therefore, they have been subject of intense research during the last decades. Recently, some research groups have shown for the palladium-hydrogen (Pd-H) system that the hydrogen atoms can trap and/or stabilize free-volume defects including those generated by plastic deformation. Deformation-induced single/double vacancies, vacancy agglomerates, dislocations and crystallite boundaries are worth considering as such free-volume defects. Furthermore, few studies observed also a hardening effect as a consequence of the hydrogen-mediated trapping and stabilization of such lattice defects, but so far no clear analyses of the defects' types nor of their specific hardening mechanisms were done.

Therefore it was the aim of this PhD thesis to carefully re-examine the reported raises in defect densities especially with respect to new deformation methods such as Severe Plastic Deformation (SPD), and analyze any effect to mechanical properties caused by hydrogenation. For this purpose commercially pure Pd was electrochemically hydrogenated up to various hydrogen concentrations, and subsequently processed by High Pressure Torsion (HPT), and cold rolling (CR) for the sake of comparison with the literature. Differential Scanning Calorimetry (DSC) was applied to differently deformed samples for detecting the deformation-induced lattice defects, particularly single/double vacancies and vacancy agglomerates. In parallel, isochronal studies of X-ray Line Profile Analysis (XLPA) were performed to explore the presence and annealing of dislocations, as well as of the thermally induced changes of crystallite size. In parallel, too, isochrones of microhardness were taken to investigate the individual effects of deformation-induced defects to the macroscopic materials' strength.

In the hydrogenated HPT-processed materials, as a function of hydrogen content, stabilization of single/double vacancies occurred; most significantly, a strong formation of vacancy agglomerates was observed, but no significant increase of dislocation density. The decrease in the crystallite size (if any) was small. The formation of vacancy agglomerates seems to be responsible for the marked anneal hardening reflected by microhardness isochrones which occurred at about the same isochrone temperature. In contrast to literature on small deformation, these results were confirmed by the investigations of cold rolled materials although the defect densities and vacancy agglomeration hardening were much smaller because of restricted deformation strain.

Recent literature documented that the effects of the Pd-H system with

respect to enhanced defect densities can be found also in the iron-carbon (Fe-C) system with C taking the role of H. Thus it was an additional aim of this thesis to find evidence for that analogy for the case of deformation-induced defects. Powders of ball milled Fe and Fe0.8wt%C were consolidated and subsequently deformed by HPT. Like in the case of Pd-H, the obtained samples were subjected to successive isochronal annealing treatments and studied by DSC, XLPD and microhardness. Again, the most apparent effect of C has been the stabilization of vacancy agglomerates with concentrations being up to a factor 10 larger in HPT-processed Fe-C than in pure Fe. The same is true for the HPT-induced single/double vacancies, while the densities of dislocations and crystallite boundaries are much less affected by the presence of C. Generally, the stabilization of deformation-induced defects was significantly stronger in Fe-C than in Pd-H because of the higher ratio of atomic radii of additional and matrix metal. Again the formation of vacancy agglomerates led to a marked anneal hardening effect which, however, was more pronounced in Fe-C than in HPT-processed Pd-H. Extraordinarily high concentrations/densities of deformation induced single/double vacancies, and vacancy agglomerates were detected in the ball-milled materials probably because of the multidirectional character as well as of the high deformation degree of ball milling.

In sum, this thesis has clearly shown that in alloys the non-dominant component can significantly decrease the surface energy of lattice defects and thus increase their thermal stability, in good accordance with the recent model created by R. Kirchheim.

Kurzfassung

Da Metall-Wasserstoff-Systeme (M-H) unter anderem die Fähigkeit besitzen, Wasserstoff (H) vorübergehend zu speichern, gelten sie als sicherer Energieträger der Zukunft. Daher wurden sie in den letzten Jahrzehnten intensiv erforscht. Kürzlich haben einige Forschungsgruppen für das Palladium-Wasserstoff-System (Pd-H) gezeigt, dass die Wasserstoffatome Defekte mit freiem Volumen einfangen und/oder stabilisieren können, einschließlich solcher, die durch plastische Verformung erzeugt werden. Deformationsinduzierte Einzel-/Doppelleerstellen, Leerstellenagglomerate, Versetzungen und Kristallitgrenzen sind als solche Defekte mit freiem Volumen in Betracht zu ziehen. Darüber hinaus beobachteten nur wenige Studien einen Härtungseffekt als Folge des durch Wasserstoff verursachten Einfangens und Stabilisierens solcher Gitterdefekte. Bisher wurden jedoch keine klaren Analysen der Defekttypen oder ihrer spezifischen Härtungsmechanismen durchgeführt.

Ziel dieser Doktorarbeit war es daher, die berichteten Erhöhungen der Defektdichten insbesondere im Hinblick auf neue Verformungsmethoden wie z.B. die starke plastische Verformung (SPD) sorgfältig zu untersuchen und die Auswirkungen der Hydrierung auf die mechanischen Eigenschaften zu analysieren. Zu diesem Zweck wurde kommerziell reines Pd bis zu verschiedenen Wasserstoffkonzentrationen elektrochemisch hydriert und anschließend zum Vergleich mit der Literatur mittels Hochdrucktorsion (HPT) und Kaltwalzen (CR) verformt. Differenz-Kalorimetrie (DSC) wurde auf unterschiedlich deformierte Proben angewendet, um die durch Deformation induzierten Gitterdefekte, insbesondere Einzel-/Doppelleerstellen und Leerstellenagglomerate, nachzuweisen. Parallel dazu wurden isochrone Studien mittels Röntgenlinienprofilanalyse (XLP) durchgeführt, um die Präsenz und das Ausheilen von Versetzungen sowie der thermisch induzierten Änderungen der Kristallitgröße zu untersuchen. Parallel dazu wurden auch Mikrohärte-Isochronen aufgenommen, um die individuellen Auswirkungen verformungsinduzierter Defekte auf die makroskopische Festigkeit der Materialien zu untersuchen.

In den hydrierten HPT-prozessierten Materialien trat in Abhängigkeit vom Wasserstoffgehalt eine Stabilisierung von Einzel- bzw. Doppelleerstellen auf. Am signifikantesten war eine starke Bildung von Leerstellenagglomeraten zu beobachten, jedoch keine signifikante Zunahme der Versetzungsdichte. Die Abnahme der Kristallitgröße (falls vorhanden) war gering. Die Bildung von Leerstellenagglomeraten scheint für die markante Zunahme der Festigkeit verantwortlich zu sein, die sich in den Mikrohärte-Isochronen widerspiegelt und die bei etwa derselben Isochronentemperatur auftrat. Im Gegensatz zur Literatur für kleine Deformationen wurden diese Ergebnisse von Un-

tersuchungen an walzdeformierten Materialien bestätigt, obwohl die Defektdichten und die Härtung der Leerstellenagglomeration aufgrund der vergleichsweise kleinen Verformung deutlich geringer waren.

Neuere Literatur dokumentiert, dass die im Pd-H-System beobachteten erhöhten Defektdichten auch im Eisen-Kohlenstoff-System (Fe-C) zu finden sind, wobei C die Rolle von H übernimmt. Daher war es ein zusätzliches Ziel dieser Arbeit, Hinweise für diese Analogie für den Fall von verformungsbedingten Defekten zu finden. Pulver aus kugelmagemahlenem Fe 0,8Gew.-% C und Fe wurden konsolidiert und anschließend durch HPT verformt. Wie im Fall von Pd-H wurden die erhaltenen Proben isochronen Glühbehandlungen unterzogen und mittels DSC, XLPa und Mikrohärte untersucht. Abermals war der offensichtlichste Effekt von C die Stabilisierung von Leerstellenagglomeraten, wobei die Konzentrationen in HPT-prozessiertem Fe-C bis zu einem Faktor 10 höher waren als in reinem HPT-prozessiertem Fe. Gleiches gilt für die HPT-induzierten Einzel-/Doppelleerstellen, während die Dichten der Versetzungen und Kristallitgrenzen durch die Präsenz von C wesentlich weniger beeinflusst werden. Im Allgemeinen war die Stabilisierung der verformungsinduzierten Defekte in Fe-C stärker ausgeprägt als in Pd-H, nicht zuletzt wegen des höheren Atomradiusverhältnisses von Zusatz- und Matrixmetall. Abermals führte die Bildung von Leerstellenagglomeraten zu einem deutlichen Härtungseffekt, der ebenfalls in HPT-prozessiertem Fe-C größer ausfällt als im HPT-prozessiertem Pd-H. Außergewöhnlich hohe Konzentrationen von verformungsinduzierten Einzel-/Doppelleerstellen und Leerstellenagglomeraten konnten in den kugelmagemahlenen Materialien nachgewiesen werden, was mit dem multidirektionalen Charakter und den extrem hohen Verformungsgraden des Kugelmahlens erklärt werden kann.

In Summe hat diese Dissertation gezeigt, dass in Legierungen die nicht dominante Komponente die Oberflächenenergie von Gitterdefekten deutlich senken kann und dadurch ihre thermische Stabilität erhöht. Dies ist in guter Übereinstimmung mit einem in jüngerer Zeit vorgestellten Modell von R. Kirchheim.

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We must find time to stop and thank
the people who make a difference in our lives.
[John F. Kennedy]

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Chapter 1

Introduction

1.1 Hydrogenated Palladium (the Pd-H system)

Investigations on metal-hydrogen (M-H) systems have got popular since the pioneering work of Thomas Graham (1805-1869) in the middle of the nineteenth century [1]. Due to the rapid diffusion of dissolved hydrogen (H) in solid metals, these M-H systems have been studied as model alloys as solid state reactions are generally very fast [2]-[8]. The probably most extensively investigated M-H system is the palladium-hydrogen (Pd-H) system since H has a significantly high solubility in Pd and an excellent ab- and desorption kinetics already at room temperature (RT), i.e. $RT = 296$ K.

Pd is a rare silvery-white metal of the platinum group. Some of its important properties are listed in table 1.1 . Since Pd does not react with oxygen at standard temperature it tarnishes not in air. Nevertheless it may tarnish at elevated temperatures.

atomic number	crystal structure	melting point T_m [K]	density $[kg\ m^{-3}]$
46	fcc	1828	12023
microhardness [GPa]	Young's modulus [GPa]	poisson ratio ν	molar mass $[kg\ mol^{-1}]$
0.5	117	0.39	106.42×10^{-3}

Table 1.1: Some important properties of Pd [9][10]

H, on the other hand, is a non-toxic but combustible diatomic gas. The most notable property of H_2 in metallurgy is its capability for embrittlement

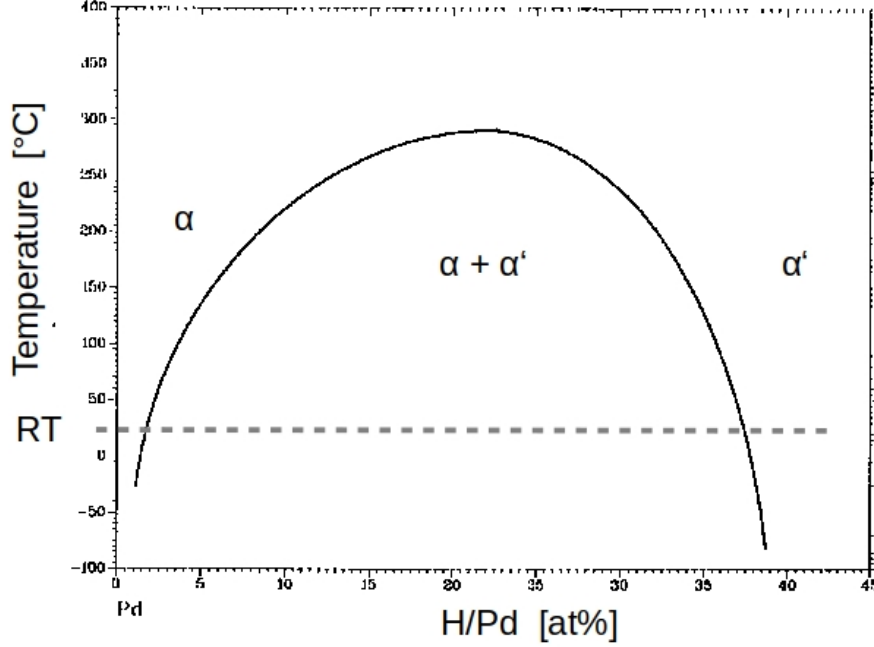


Figure 1.1: Phase diagram of the Pd-H system, after [11]

of many metals and, in general, the potential to be an energy carrier of the future. For the diffusion process it is necessary to dissociate the hydrogen molecules into atomic H. Pd in turn can act as a catalyst for this reaction which was published countless times.

The phase diagram of the Pd-H system is sketched in fig. 1.1 showing three phases, i.e. α , α' and $\alpha + \alpha'$ where the α -phase is associated with a non-stoichiometric interstitial solid solution of H in Pd (Hägg phase) while the α' -phase represents the stoichiometric hydride phase [11] [55]. The α -phase exhibits a lattice parameter of $a(\alpha) = 0.3887 \text{ nm}$ while the α' -phase is indicating one of $a(\alpha') = 0.4025 \text{ nm}$. During sample preparation (see chapter 5.2) the hydrogenation was chosen so that at least one H concentration (H/Pd) of each phase at room temperature was realized, i.e. $(\frac{H}{Pd})_{\alpha} \lesssim 0.017$, $(\frac{H}{Pd})_{\alpha'} \gtrsim 0.37$ and $0.017 \lesssim (\frac{H}{Pd})_{\alpha+\alpha'} \lesssim 0.37$.

In 2010 a significant increase in the densities of lattice defects, i.e. vacancies and dislocations, in a hydrogenated Pd (Pd-H) subjected to Severe Plastic Deformation (SPD) was found [12]. Further investigations observed a tremendous increase in the macroscopic strength due to such an increased defect densities [13]. To explain this observation two different strengthening

mechanisms, i.e. vacancy (Vac) hardening or dislocation hardening, have been supposed. It is assumed that the gain in macroscopic strength is a result of a stabilization of deformation-induced lattice defects through the absorbed H.

1.2 Carbonized Iron (the Fe-C system)

Nanostructured iron (Fe) alloys are used in numerous applications. They can be used as nanoparticles for ultrahigh density magnetic recording [15], as nanocrystalline powder cores for high frequency applications [16], as heat- and radiation resistant reactor materials [17] or as biodegradable cardiovascular stents [18] to name but a few. Recently it has been demonstrated that nanocrystalline, low-C steel can be prepared by mechanical alloying of Fe and graphite [19]. Grain sizes varying from 5 to 15 nm were reported. This extraordinary small grain size is a result of the interaction of solute elements, namely carbon (C), with the grain boundaries in low-C steel obtained by mechanical alloying.

It is supposed by Kirchheim that an excess of a different substance at boundaries in a metal can reduce the energy of such a boundary which leads to a reduced driving force for their annihilation [20][21]. Kirchheim called such a different substance a defactant (defect acting agent). Based on this defactant-concept one can hypothesize that C can act in Fe in the same way as H does in palladium (Pd), i.e. C is a defactant in Fe and can trap lattice defects. This is a hypothesis which has to be investigated intensively.

The Fe-C system that was used in this work is Fe0.8wt%C. The melting point of Fe0.8wt%C can be found with sufficient accuracy in every iron-carbon-phase diagram. The important properties of this low C steel are listed in table 1.2. The molar mass of pure Fe can be taken as a good approximation for that of Fe0.8wt%C.

atomic numbers	crystal structure	melting point T_m [K]	density [kg m ⁻³]
26 and 6	bcc at RT	1739	7750 ... 8080
microhardness [GPa]	Young's modulus [GPa]	poisson ratio ν	molar mass (pure Fe) [kg mol ⁻¹]
0.22 ... 6.48	183 ... 213	0.29	55.85×10^{-3}

Table 1.2: Important properties of Fe0.8wt%C [9][10]

1.3 Severe Plastic Deformation (SPD)

Materials with reduced grain sizes below 100nm, i.e. nanocrystalline materials, show different mechanical, electrical, thermodynamic and magnetic properties than their coarse grained counterparts [22]. Therefore they are of great technological interest. So far two different processing strategies have been followed for the production of nanocrystalline materials: bottom-up and top-down approaches [23].

In the bottom-up approach ultrafine powders consisting of nanocrystalline particles are produced. Some examples of techniques for this approach are ball milling (BM) and inert gas condensation [24]. Coatings or nanocrystalline films consisting of grains with sizes below 100nm can be deposited by electrodeposition or vapor phase deposition [25]. A consolidation of these ultrafine powders by subsequent compression provides bulk samples but with compromises in density with poor inter-particle bonding and in grain size. In particular porosity may lead to a significant loss in fracture toughness and ductility.

In the top-down approach a bulk material consisting of coarse grains is nanostructured by refining the grains down to the nanometer scale without significant changes in the sample shape. Severe Plastic Deformation (SPD) provides the most powerful tools for nanostructuring coarse grained bulk materials by a large variety of methods [26][27]. Moreover, there is a number of features that can only be achieved by materials subjected to SPD. These are (i) a considerable ductility, (ii) an enhancement in diffusion and (iii) changes in phase stability [14]. Comparing the nanostructure of SPD processed materials with those achieved by other methods it has been shown that deformation-induced lattice defects are specific of SPD [14]. The common principle of all SPD techniques is that materials are severely deformed at relatively low homologous temperatures and under high hydrostatic pressure. Today, the most prominent SPD techniques are Equal-Channel Angular Extrusion [28], Accumulative Roll-Bonding [29][30] and High Pressure Torsion (HPT) [31]. In addition, it is well known that large strain deformations can result in a remarkable refinement of the microstructure at low temperatures [32]. A medium or even large strain deformation can be realized by drawing or Cold Rolling (CR). However, these above mentioned methods show large differences in their capabilities (i) to form commercial shape bulk nanocrystalline materials, (ii) achieving small grain sizes, (iii) to create deformation-induced lattice defects and (iv) to achieve considerable misorientation angles by grain boundaries.

For this thesis High Pressure Torsion (HPT) was applied as SPD method on

the Pd-H, since it is a powerful tool to produce high densities of deformation-induced lattice defects at minimum grain size. This is due to a two-fold effect of the hydrostatic pressure: it prevents crack formation and suppresses annihilation of deformation-induced lattice defects.

A second part of this work deals with Cold Rolling on the Pd-H system. Here the capability of nanostructuring and producing deformation-induced lattice defects is much smaller than for HPT, due to much smaller deformation degrees. This will lead to a comparison in the capability of stabilization of deformation-induced lattice defects.

Ball milling was used followed by a consolidation under high pressure and subsequent deformation by HPT for the Fe-C system to produce samples of low-C steel. The method itself is well established for various different metals, e.g. for Ti [33], Co [34], Cu [35] or Fe1wt%C [36].

1.4 Preliminary remark

The terms XRD, i.e. X-Ray Diffraction, and XLPA, i.e. X-Ray Line Profile Analysis, are used not uniformly in literature. In this thesis the expressions XRD is used for the procedure of recording a X-ray diffraction pattern and XLPA for the process of evaluation and analysis of such recorded diffraction pattern, respectively. Furthermore, the terms "domain-", "crystallite-" and "coherently scattered domain- (CSD)" size are used often synonymously. In order to avoid a lack of clarity the terms "crystallite" and "crystallite size", respectively, are used within the framework of this work and explained in chapter 5.

Chapter 2

State Of The Art

2.1 The Pd-H system

In 1993 and 10 years later Fukai showed in a series of experiments that vacancies and vacancy-clusters can be formed in very high concentrations (i.e. up to 16%) in various quenched M-H systems. This is because vacancies and vacancy-clusters get easily trapped by the solute H atoms [5][40]. He also demonstrated that these high numbers of vacancies can arrange to even ordered vacancy sublattices [40][41]. In 2000 Fukai et al. reported concrete values for the formation enthalpy of a monovacancy in Pd and the formation energy of a vacancy-H cluster [42]. Vekilova et al. carried out in 2009 first principle studies of the effect of H in Pd by Density-Functional-Theory simulations [43]. They found that it is energetically more favorable to fill a mono-vacancy with H atoms than with H molecules. Moreover they found a maximum number of 6 H atoms per vacancy. It should be noted that all these investigations mentioned above deal with **thermally induced** vacancies and **not with deformation-induced** vacancies; giving some motivation for the current thesis.

The first author who dealt with deformation induced lattice defects was Krystian et al. in 2010 [12]. In 2011 Bönisch et al. found a stabilization of deformation-induced mono-vacancies in Pd-H by forming vacancy-H complexes [46]. They detected it by a peak shift in measurements with Differential Scanning Calorimetry (DSC) which is indicated by blue arrows in fig. 2.1. Čížek et al. confirmed in 2015 the stabilization of deformation-induced mono-vacancies by finding vacancy-H complexes [47]. However, they confirmed this for Pd thin films and not for bulk materials. In 2015 Deutges et al. investigated homogeneous dislocation structures in a cold rolled Pd [48]. They found a change of the size of dislocation cells and subgrains with

increased H concentration.

Of crucial importance for this work are the four publications [12]-[14] and [37]. They will be discussed in detail in the following.

Setman et al. in 2008 as well as Krystian et al. in 2010 reported high concentrations of superabundant vacancies and a high thermal stability of vacancies and vacancy agglomerates due to H in HPT-processed Pd [12][14]. Fig. 2.1 demonstrates DSC curves of a HPT-processed Pd-H sample in comparison to a HPT-processed, non-hydrogenated one. A very sharp strong peak at 482 K could be observed for the Pd-H sample, in contrast to the sample deformed without H where only a tiny peak was found at 373 K. The peak was identified to come from annealing of vacancy-H clusters. Krystian et al. and Setman et al. ascribed this shift in peak temperature to a trapping of mono-vacancies by solute H [12][14]. Through this trapping the concentration of vacancies was increased by three orders of magnitude in case of the hydrogenated HPT-processed palladium. A similar stabilization they found with the dislocation annealing peak being around 522 K with the non-hydrogenated palladium but as high as 676 K with the hydrogenated one. An increase in dislocation density, however, in this sample was not observed. In a SEM investigation in parallel to the DSC they found clear evidence for the presence of pores (fig 2.2) which they interpreted to have formed from the vacancy-H clusters which were found by combined evaluation of DSC and TEM.

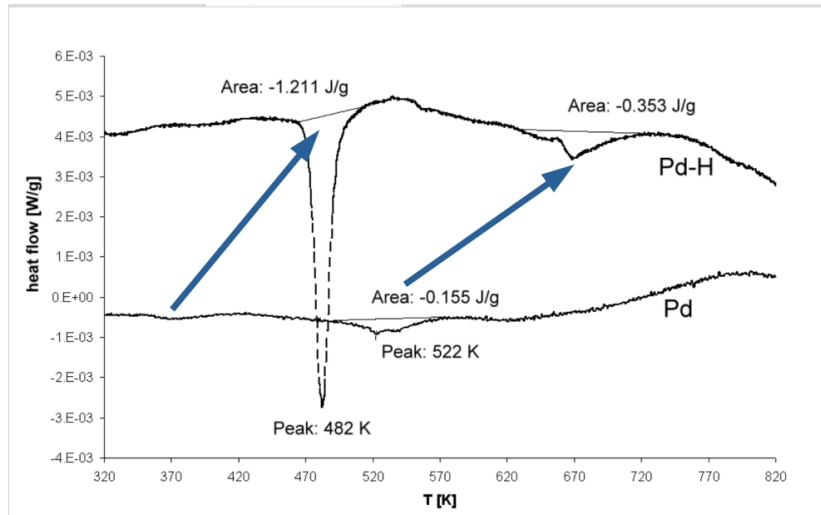


Figure 2.1: DSC plot of HPT-processed Pd with H (upper curve) and without H (lower curve) to demonstrate trapping of defects by solute H [14]

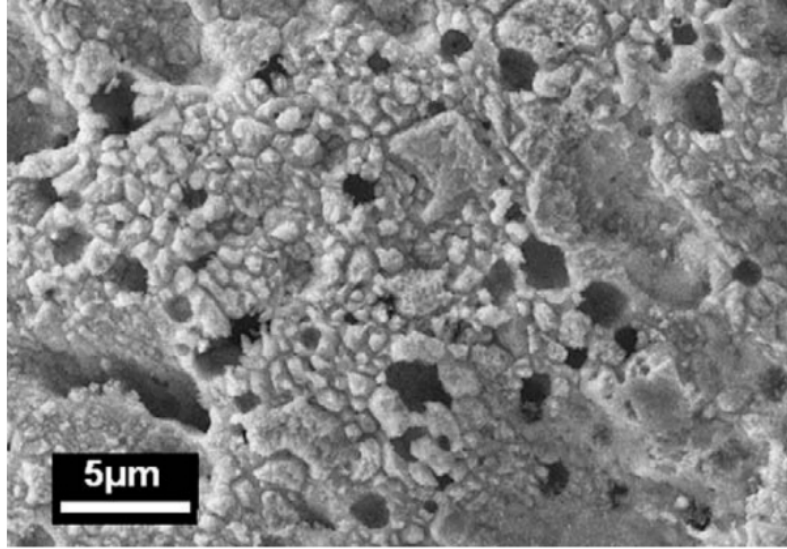


Figure 2.2: SEM picture of Pd-H after HPT and additional heat treatment [12]

In 2013 Chen et al. reported an increase in dislocation density in cold rolled (CR) Pd-H compared to the dislocation density after CR of pure Pd [13]. The reason that this finding does not agree with the finding of Setman et al. [14] and Krystian et al. [12] may lie in the fact that Chen et al. did not remove the interstitially solved hydrogen before deformation [13]. They also achieved microhardness measurements (see fig. 2.3) which show a marked increase with increasing hydrogen content. However, the yield strength was similar for all hydrogen concentrations meaning that the increasing hydrogen content only contributes to the strain hardening coefficient and not to the yield strength. Chen et al. concluded that in cold rolled Pd-H the observed increase of dislocation density with increasing H concentration is caused by an enhanced ability of dislocation multiplication.

In 2015 Chen et al. again investigated the nature of hardening effects of H on Pd, this time by tensile tests arranged directly within the electrolyte hydrogen loading system [37]. Again, they found that H enhances the strain hardening of Pd significantly while the yield strength is not affected. It is worth noting that also in this study the H was not removed before the mechanical measurements! This is in strong contrast to the investigations of Setman et al. [14] and Krystian et al. [12] where in all cases the hydrogen was removed immediately after the deformation treatment as it has been also done throughout this work.

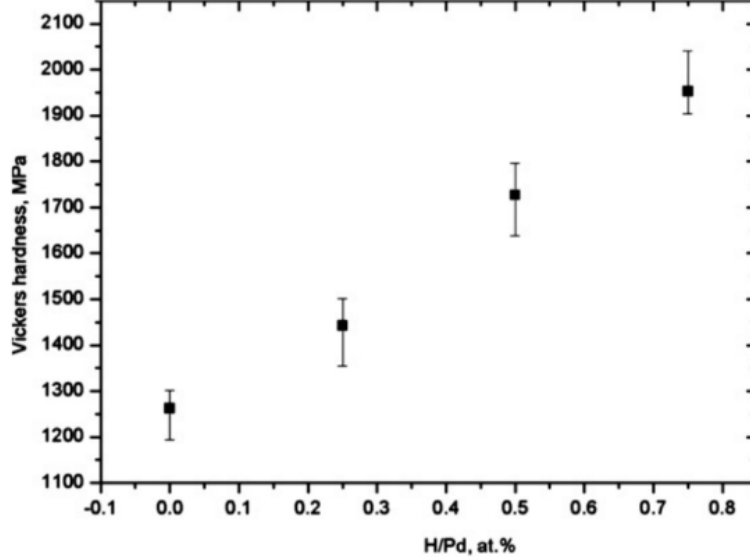


Figure 2.3: Measured Vickers hardness (microhardness as function of the pre-charged H concentration [13])

2.2 The Fe-C system

A few investigations on SPD processing, namely HPT, of C-steels of various compositions and their microstructural and mechanical properties have been already conducted [49]-[53]. A common result of all these researches is an increase of the initial hardness by a factor of 2.5 - 6 due to HPT processing. Additionally, Zrinc et al. studied the influence of the deformation parameters of HPT on the properties of a medium C-steel [49]. There were also investigations by Todaka et al. on the microstructure and mechanical properties of pure Fe subjected to HPT [51]. They observed elongated grains and a very high ultimate tensile strength (UTS) which they ascribed to partial grains with low dislocation density.

In 2003 Ivanisenko et al. analyzed the nanostructure and phase composition [52] as well as the influence of annealing on structure and phases [53] in a commercial pearlitic steel deformed by HPT. They found a grain refinement down to 10 nm grain size combined with a HPT-induced increase in hardness up to 11 GPa. Furthermore, an enhanced thermal stability was observed. During a strain-induced dissolution of cementite, Ivanisenko et al.

registered a drag of C atoms within the ferrite matrix. They identified this flow of C atoms as a mechanically driven mass transport which can be qualitatively described by mechanical diffusion parameters. Moreover, they found a formation of nanostructures with dissolved C without changes in lattice parameters. Additionally, they observed C atoms located in dislocation cores. In 2014 Borchers et al. studied point defect populations in cold-drawn wires of Fe0.8wt%C (and other alloying elements) [54]. They found vacancy-clusters which consisted of 9 to 10 vacancies. Vacancies (Vac) were trapped by the C-atoms in form of Vac_1C_2 - or/and Vac_2C_4 -clusters led to vacancy concentrations of at least $c_{Vac} > 10^{-6}$ mostly to the order of typically 10^{-4} . Furthermore, they calculated the formation enthalpy of a deformation-induced mono-vacancy in Fe0.8wt%C to be $\Delta H_v^f \approx 0.28 \text{ eV}$. This very low value was explained with a strong reduction of the vacancy formation enthalpy by the defectants, i.e. C in Fe via trapping of vacancies. It should be noted that all these investigations [49]-[53] concerned **bulk nanocrystalline** Fe-C alloys. Therefore the results of Ivanisenko et al. have to be considered critically when comparing them with the results of this work, where ball milled nanocrystalline Fe 0.8wt%C powders have been consolidated before investigation.

Chen et al. produced powders of Fe-C alloys with different C contents in 2013 [19]. They performed microstructural analyses by XRD and TEM as well as an analysis of the C distribution by Atom Probe Tomography (APT). A dislocation density in the order of $10^{16}m^{-2}$ was found. The grain size was observed to be significantly reduced down to 6 nm and this was explained by a segregation of C atoms from the grain interior into the grain boundaries. This segregation of C atoms was found to be independent of the grain size.

Of crucial importance for this thesis are the two publications [36] and [39] which will be discussed now in detail in the following.

In 2002 Ivanisenko et al. investigated compacts of nanocrystalline Fe1.0wt%C powders produced by mechanical alloying and consolidation by HPT [36]. The grain size of the compacts was 6 - 10 nm. The microhardness of the pre-compressed powder was 8.5 GPa. Subsequently the samples were deformed by HPT. Fig. 2.4(a) is visualizing the stress-strain curve obtained by three-point-bending. The slope of the stress-strain curve was estimated to represent a Young's modulus of 210 GPa, which is slightly smaller than that of coarse grained carbon steel of the same composition. Fig. 2.4(b) depicts the crystallite size and the microhardness achieved by HPT and their behavior with thermal treatment at several temperatures till $900^\circ C$. Obviously primary recrystallization sets in at $\sim 700^\circ C$. Furthermore, Ivanisenko et al. monitored coherent precipitates of carbides inside grains. After HPT

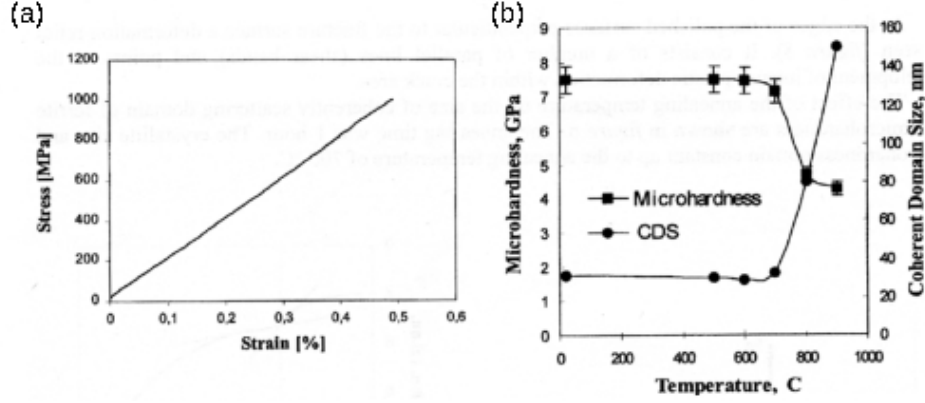


Figure 2.4: Nanocrystalline and consolidated Fe1.0wt%C. (a) Stress-strain curve of the Three-Point-Bending Test (b) Microhardness and CDS/crystallite size during annealing [36]

they evaluated a CDS of 30 nm using the Warren Averbach method. Of special interest is that they registered the microhardness after BM and pre-compression (but before HPT!) to decrease by 12% on a value of 7.5 GPa after HPT. Compliant with this finding they measured the grain size to increase from 10 nm after BM but before HPT to a value of 70 nm after HPT. Ivanisenko et al. did not comment on this observation but it is not surprising since both procedures, ball milling (BM) as well as High Pressure Torsion, represent techniques of plastic deformation. In BM the strain is applied by three directions while the strain in HPT comes from shear deformation, and therefore the deformation in ball milling is more pronounced resulting in smaller grain sizes and higher microhardness values. Ivanisenko et al. also showed that ball milling allows for mechanical alloying of the components Fe and C that is achieving a solid solution of Fe1wt%C in spite of the natural solubility of C in α -Fe being (~ 0.001 wt% at RT). It should be mentioned that also the consolidation by HPT processing is capable of mechanical alloying up to this concentration.

Borchers et al. studied compacts of steel powders by BM/mechanical alloying and consolidated by HPT of Fe0.4wt%C [39]. The thermal and mechanical properties of these compacts were investigated. Similarly as by the work of Ivanisenko [36], a nanocrystalline structure with grain sizes around 10 nm was achieved. After applying HPT, the structure was still body-centered-cubic (bcc) with a solid solution Fe-C of Fe0.4wt%C. With increasing HPT strain the microhardness increased from 7.2 to 12.6 GPa.

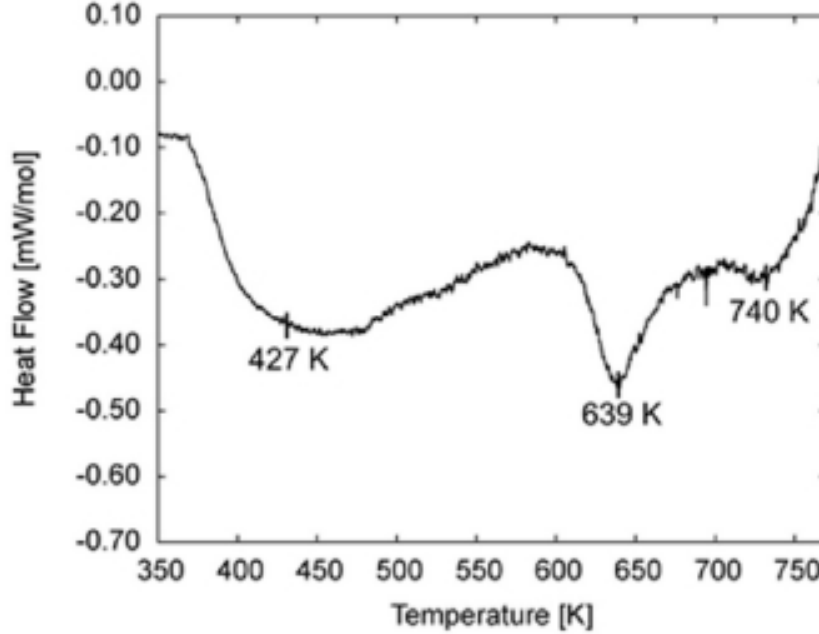


Figure 2.5: DSC plot obtained from compacts of Fe_{0.4}wt%C [39]

The strain applied was large enough to reach saturation in microhardness, i.e. a constant value of microhardness over the whole samples' cross-section as a consequence of an overall homogenous nanostructure. In parallel to the microhardness tests tensile tests were performed showing an UTS of 80 MPa. like in the case of Ivanisenko [36] a strong discrepancy between UTS and microhardness was found. Interestingly, Borchers et al. also performed DSC investigations at the ball milled and HPT processed samples. The results are demonstrated in fig 2.5. They found several exothermic and one endothermic peak at 427 K, 577 K, 639 K and 740K and interpreted them (in series starting with the lowest temperature) as the annealing of mono-/di-vacancies, Vac_1C_2 or Vac_2C_4 agglomerates, and as the onset of grain coarsening at the highest annealing peak temperature observed. The concentration of the vacancies found was of the order of 10^{-4} . Another result concerns an increase in grain size from 10 nm of the powder after BM (before HPT) to 20 nm of the compact after HPT. They explained this increase with quite different strain rates of BM and HPT (5 orders of magnitude!). This effect will be also subject of the current work.

Borchers et al. found another evidence for the significant presence of the vacancy-type defect from lattice parameter data which showed no difference

to that of pure Fe. They suspected that the lattice extension due to C is compensated by a lattice contraction due to vacancy-type defects.

Chapter 3

Aims of Research

The aim of this doctoral thesis was to investigate the impact of defactants on deformation-induced lattice defects in metals. Two different systems of metal-defactant were chosen, i.e. the Pd-H system and the Fe-C system. For this purpose, already published work was taken up and expanded to the question of the impact of defactants for SPD-induced defects.

3.1 The Pd-H system

In fig. 2.1 a stabilization of SPD-induced lattice defects is seen [14]. Moreover, a significant increase in the macroscopic strength in the Pd-H system due to lattice defects was observed [13][37]. Different explanations for these observations have been published. The aim of this part of the thesis was to analyze systematically the supposed stabilization of lattice defects and the extra strength arising from hydrogenation and SPD. Therefore several questions had to be answered:

- Can vacancies, dislocations and crystallite boundaries be trapped/ stabilized by H as a defactant in Pd?
- What is the impact of vacancies and/or vacancy-agglomerates on the macroscopic strength?
- What is the impact of dislocations on the macroscopic strength in this system?
- What is the influence of crystallite boundaries and grain boundaries, respectively, on the macroscopic strength?

- How important is the initial H concentration in Pd for the stabilization of deformation-induced lattice defects?
- How important is the degree of deformation for the stabilization of dislocations, vacancies and crystallite boundaries?
- Is there an influence of the SPD processing temperature?

3.2 The Fe-C system

It is published that C acts as a defactant in a C-rich cold-drawn pearlitic steel wire and therefore stabilizes dislocations [38]. Additionally it has been published that C traps vacancies in nanocrystalline low-C steel obtained by BM and subsequent consolidation [39]. The aim of this part of the thesis was to clarify the following issues :

- Can vacancies, dislocations and crystallite boundaries be stabilized by C as a defactant in Fe?
- How large is the impact of stabilized vacancies and/or vacancy agglomerates on the macroscopic strength in this system?
- How large is the impact of stabilized dislocations on the macroscopic strength?
- Is there an influence of crystallite boundaries and grain boundaries, respectively, on the macroscopic strength?
- What is the influence of the parameters of consolidation and deformation on the densities of lattice defects?

Chapter 4

Theoretical Background

4.1 Defects in metals

In all crystalline solids the atoms arrange in a very regular sequence, the crystal lattice. For thermodynamic reasons, at $T > 0K$ deviations from the ideal crystal occur which are called defects [55]. Such defects have a tremendous impact on the macroscopic properties of the material since they distort the unstressed lattice. Usually defects are classified by their dimension.

0-dimensional point defects: These are defects which have the extension in space of exact one atom. Examples of point defects are vacancies, interstitials and substitutional atoms.

1-dimensional line defects: Defects caused by a misalignment of atoms of the crystal lattice are classified as line defects. Dislocations are exemplars of 1-dimensional defects.

2-dimensional planar defects: deviations of the ideal lattice appearing in a lattice plane or at a surface are categorized as planar defects. Phase and grain boundaries as well as stacking faults represent these defects.

3-dimensional bulk defects: These defects are extended to a volume inside the crystal. Examples are voids, especially vacancy-agglomerates, and precipitates.

Essential for this thesis are vacancies, dislocations, grain boundaries and vacancy-agglomerates which will be discussed now in detail in the following.

4.1.1 Vacancies

When an atom is missing from its regular site in the crystal structure a vacancy is produced [56]. Although vacancies are classified as point defects their disruption of the crystalline structure affects several atoms distances. Fig. 4.1 visualizes the most important point defects. In Fig. 4.1(a) a mono-vacancy can be seen. The disturbance of a mono-vacancy on the crystal lattice is sketched by curved lines between the atoms. Fig. 4.1(b) shows an interstitial atom (red) and its typical impact on the crystal structure. A small substitutional atom and a large one, respectively, are illustrated in fig. 4.1(c) and (d). Substitutional atoms can be interpreted within the defectant model of Kirchheim [20][21] as atoms of a defectant trapped by a vacancy as was found for Pd-H [12][14] as well as for Fe-C [39].

In the presence of vacancies the thermodynamic stability is increased due to

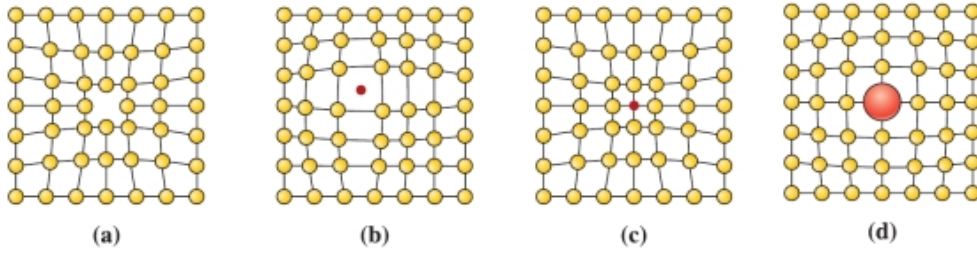


Figure 4.1: Overview of important point defects in metals. (a) vacancy, (b) interstitial atom, (c) small substitutional atom, (d) large substitutional atom [56]

an increase in the entropy of the material [56]. A vacancy is introduced into a metal by plastic deformation, at high temperature, during solidification, or by radiation damage. In diffusion processes vacancies are of crucial importance, especially in pure metals. In thermal equilibrium the concentration of thermally-induced vacancies is determined by an Arrhenius type relation up to the melting point by

$$c_{Vac} = N \exp\left(-\frac{\Delta H_v^f}{k_B T}\right) = \frac{m N_A}{V M} \exp\left(-\frac{\Delta H_v^f}{k_B T}\right) \quad (4.1)$$

where c_{Vac} is the vacancy concentration, N denotes the concentration of atomic sites in the crystal lattice, ΔH_v^f presents the formation enthalpy of a thermally-induced mono-vacancy, k_B is the Boltzmann constant, T is the absolute temperature, $\frac{m}{V}$ denotes the materials' density, N_A is the Avogadro

constant and M presents the molar mass. It has to be noted that deformation-induced vacancies, especially when deformed by SPD, are superabundant [12][14] and therefore in a highly non-equilibrium state in relation to the thermally induced ones.

It is possible to measure vacancies by all kinds of isochronal experiments. One is the measurement of the resistivity during successive heat treatment since point defects lead to an increase in resistance until they are annealed [55]. A second concept is a DSC measurement. Vacancies can be verified by an exothermic peak in the obtained DSC plot at approx. $0.2T_m$ with T_m being the melting temperature [12][57][59]. A third method is dilatometry where in parallel the changes in length and in lattice parameter during isochronal heating are investigated to detect vacancies [55] [60].

4.1.2 Dislocations

A dislocation is a line defect around which some of the atoms of the crystalline structure are misaligned. Two different types of dislocations can be distinguished by their nature of misalignment: the screw dislocation, the edge dislocation and arbitrary superpositions of these [55]. The magnitude and direction of the lattice distortion resulting from dislocations is quantified by the Burgers vector b . The Burgers vector is defined as a vector between the end and starting point when orbiting the dislocation line in a square with equidistant sides in one crystallographic plane. In metals the magnitude of b is one interatomic spacing and b is aligned with close packed crystallographic directions [59]. The characteristic deformability of metals is ascribed to the presence of dislocations and their ability to move and interact under the influence of temperature or stresses induced by external loads.

In screw dislocations the Burgers vector is parallel to the dislocation line. It can be visualized by slicing midway through a defect-free crystal and distorting the crystal by one atomic spacing [56]. Two screw dislocations are called antiparallel if their corresponding Burgers vectors differ in sign, i.e. when they differ in their sense of helix. Antiparallel screw dislocations can annihilate if they coincide.

At edge dislocations the Burgers vector is perpendicular to the dislocation line. Often it is illustrated by cutting half way through a perfect crystal and inserting a half plane of atoms [56][55]. The edge dislocation is represented by the bottom edge of this inserted half plane. The lattice distortion by a edge dislocation persists in a compression of the atoms above and a stretching of atoms below the dislocation. If the corresponding Burgers vector of two dislocations differ in sign they are called antiparallel and therefore can annihilate.

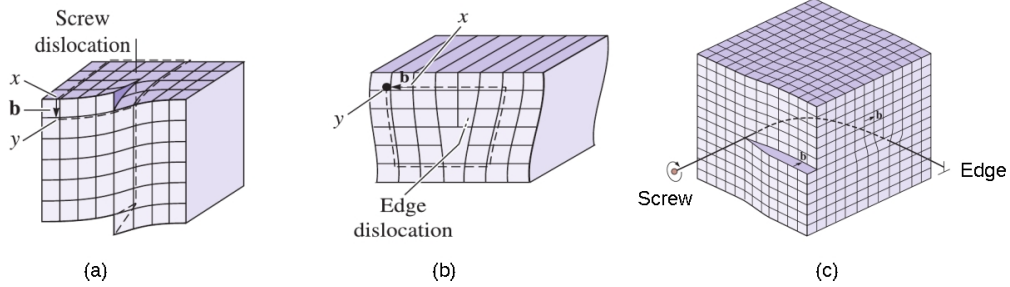


Figure 4.2: Types of dislocations: (a) a screw dislocation, (b) an edge dislocation (c) a superposition of screw and edge dislocation [56]

Fig. 4.2 is showing the two types of dislocations and a superposition of them. The line defect along which shearing occurs is a screw dislocation, see fig. 4.2(a). The Burgers vector is parallel to the dislocation line and one atomic spacing. The atoms above an edge dislocation are compressed while those below the edge are stretched, see fig. 4.2(b). Fig. 4.2(c) depicts a mixed dislocation. The edge dislocation at the side of the crystal changes to a screw dislocation at the front face of the crystal. However, the Burgers vector remains the same at all positions of the mixed dislocation.

For measuring dislocations several techniques exist. They can be observed in their atomic structure by TEM[55]. SEM investigations on etched surfaces containing dislocations show them by dark lines. A powerful tool to measure dislocation indirectly is XRD with a subsequent X-Ray Line Profile Analysis (XLPA). Here the dislocation density can be evaluated from an observed peak broadening [62] - [67]. Furthermore, also in DSC measurements dislocations can be detected since they show a characteristic exothermic peak [12][57][59].

4.1.3 Grain boundaries

The microstructure of metals consists of many grains. A grain is a section in which the lattice structure is everywhere identical [56]. Different grains in a metal have the identical lattice structure but differ in their crystallographic orientation. Grain boundaries are surfaces that separate the individual grains. Within a grain boundary the atoms are arranged randomly. It is clear that the amount of grain boundaries within a metal is proportional to the reciprocal grain size and the amount of grains, respectively. Grain boundary hardening is one important strengthening mechanism in metals. Fig. 4.3(a) visualizes the principle idea of grain boundaries. Microscopy of

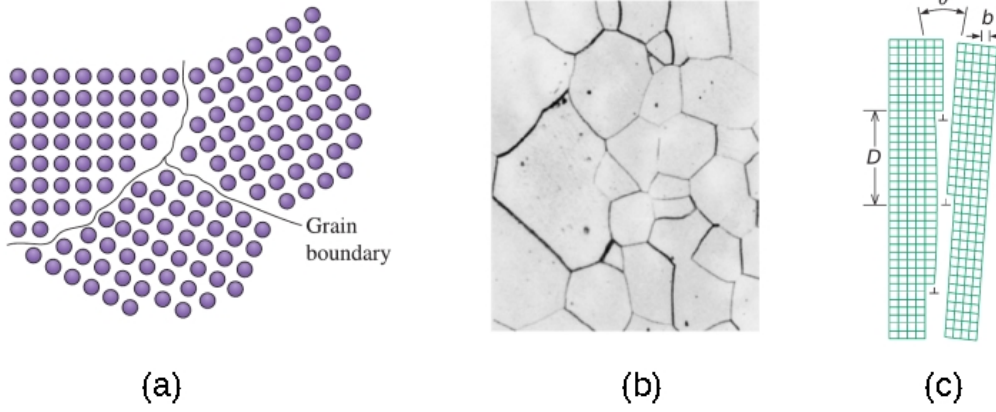


Figure 4.3: grain boundaries: (a) sketch of the atomic structure of grain boundaries (b) optical microscope image of grains and grain boundaries in Pd (c) crystallographic structure of a low angle grain boundary[56]

polished and etched samples is one possibility to observe grain boundaries. In fig. 4.3(b) one can see a typical optical microscope image of a polished and etched metal, namely coarse grained Pd, showing grains (bright) and grain boundaries in dark. Grain boundaries can be differed by their angle of misorientation between adjacent grains in high angle grain boundaries and low angle grain boundaries. An array of dislocations that produces a small misorientation between adjacent grains are called a low angle grain boundary, as shown in fig. 4.3(c). In a low angle grain boundary the dislocations have a distance to each other of $D = \frac{b}{\Theta}$ with the length of the Burgers vector b and the misorientation angle Θ [55].

Grain boundaries can be observed by microscopy (bright field TEM, SEM, optical) of polished and appropriate etched samples. By etching the grain boundaries are affected different from the grain and therefore look brighter or darker than the grain in the microscope.

It is noteworthy that grain boundaries can consume dislocations as well as point defects, namely vacancies, and therefore might reduce their densities. Furthermore, dislocations can not pass through grain boundaries so that dislocation movement is stopped in these.

4.1.4 Vacancy agglomerates

Vacancies are formed as mono-vacancies but can also be created as agglomerates of two or more vacancies. In literature one can find that a significant

fraction of vacancies is generated in agglomerates [68]. It is also possible by vacancy mobility that mono-vacancies rearrange into vacancy-agglomerates during annealing of vacancies in superabundance. As mentioned above, vacancies introduced by SPD are superabundant.

vacancy-agglomerates occur in several different configurations. Vacancies can cluster to form voids, which are common features of the microstructure. Such voids show usually a near-spherical shape with aspects on close-packed crystallographic planes since they have low surface energies [68]. Furthermore, vacancies may also agglomerate together in loose arrangements in the core of displacement cascades. Interactions of such loose vacancy-agglomerates with dislocations are relevant in hardening the matrix metal. Moreover, vacancy-agglomerates could form loops or stacking fault tetrahedrons and therefore show a dislocation-like behavior [68]. If vacancy-agglomerates form voids, especially in large agglomerates, these cavities may contain H gas when H atoms are present in the crystal.

Vacancy-agglomerates in form of voids might offer strong resistance to a dislocation strain field and therefore strengthen a metal. Depending on the size of a vacancy-agglomerate, the orientation of a moving dislocation (slip plane) and the character of the dislocation (screw, edge), four different settings are possible [68]:

- 1) The vacancy-agglomerate is crossed by the dislocation and both keep unchanged. In this setting, the vacancy-agglomerate is sheared by the dislocation but is fully reconstructed after the dislocation unpins. An additional hardening of the metal is negligible.
- 2) The void is crossed and modified by the dislocation but the dislocation itself is unchanged. Here, the void is sheared by the dislocation and this shearing keeps stable. This leads to an additional hardening effect.
- 3) An edge dislocation is absorbing (partial or full) the vacancy-agglomerate which acquires a double superjog. This setting is only relevant for large vacancy-agglomerates and high temperatures. The dislocation will be enlarged and the concentration of vacancies will be reduced leading to a decrease in hardness.
- 4) A screw dislocation absorbs the vacancy-agglomerate into a helical turn. This is the most common reaction for a screw dislocation. The impact on the hardness is the same as for 3).

If agglomerates form loose arrangements their impact on the macroscopic strength of a metal is slightly smaller than that of voids with the same number of vacancies but is still very significant [68]. On the other hand, the absorption of loose arrangements of vacancies by dislocations is a much more efficient process. Therefore it occurs for loose arrangements at lower temperature compared to voids.

The measurement of vacancy-agglomerates is possible by all kinds of isochronal investigations since their thermal stability is between that of mono-vacancies and that of dislocations, depending on size configuration of the agglomerate, i.e. single vacancy, void or vacancy loop. One approach for measuring vacancy-agglomerates is DSC where an exothermic peak at a characteristic homologous temperature can be found [12][57][59]. Another approach, for example, is an isochrone by microhardness where a change in microhardness at a characteristic homologous temperature might be observed, see section 5.3.

4.2 Defactants in metals

In 2007 Kirchheim derived the defactant-concept to explain the segregation of solute atoms around lattice defects [20][21]. A defactant is a defect acting agent in analogy to surfactants (surface acting agents) proposed by Gibbs. Since lattice defects interact attractively with solute atoms in a binary or multi-component system these solutes segregate at defects and, therefore, the total free energy is decreased. The corresponding reduction in total free energy can be related either (i) to a lowering in the energy of the trapped solute atom or (ii) to a reduction in the formation energy of the defect [20]. Based on J.W. Gibbs' well known adsorption isotherm (eq. 4.2), which is valid for surfaces and surfactants only, and using Wagner's definition of surface excess Kirchheim derived a generalized relation (eq. 4.3) for an excess of solute atoms at a lattice defect [20].

$$d\gamma = -\Gamma_A d\mu_A \quad (4.2)$$

$$\Gamma_A = \left. \frac{1}{V} \frac{\partial n_A}{\partial \rho} \right|_{T, V, \mu_A, n_B} \quad (4.3)$$

Here, Γ_A is the excess of solute atoms, $d\gamma$ denotes the change in surface energy, μ_A presents the chemical potential of the solute, V is the volume, n_A and n_B denote the number of solute (index A) and solvent atoms (index B), respectively, ρ is the defect density and T presents the temperature. In eq. 4.3 the (general) defect density ρ describes either the vacancy concentration, the dislocation density or the grain boundary area per volume, respectively, for each corresponding type of different lattice defect [20]. Fig. 4.4 depicts a schematic diagram of the trend of eq. 4.2 in dependence of the chemical potential of the solute atom μ_A [20][21]. From fig. 4.4 as well as from eqs. 4.2 and 4.3 one can see for very low values of μ_A the concentration of the

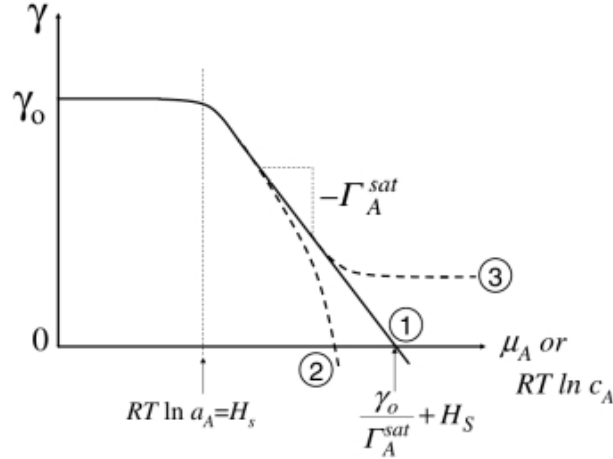


Figure 4.4: Change in defect energy γ according to eq. 4.2 with increasing chemical potential of the solute atom μ_A [20][21]

defactant (index A) in the solvent (index B) is very small and therefore the excess of the defactant Γ_A around the defect is also very small, i.e. a slight segregation of the defactant. On the other hand, at very high μ_A values the defect becomes saturated with defactants due to a limited number of segregation sites in the defect. The saturated and therefore constant excess in fig. 4.4 is denoted Γ_A^{sat} . While saturation of the defect with defactants the defect energy γ is decreasing linearly with increasing μ_A until point ①. If Γ_A is not constant but increases with increasing μ_A the decrease in the defect energy γ is even more pronounced (cf. point ②). It is noteworthy that, for thermodynamic reasons, the defect energy γ has to increase with increasing defect density ρ and, therefore, the excess of defactants Γ_A at a defect is decreased (cf. point ③) [20][21].

Of importance is the defactant-concept for understanding the impact of defactants in a metal on deformation-induced lattice defects in Pd-H as well as in Fe-C. Kirchheim's defactant-concept may matter in materials science in all circumstances where defects modify macroscopic properties. Examples, to name only a few, are:

- enhancement of substitutional diffusion via an increased c_{Vac} due to a stabilization effect of solute segregation on vacancies
- inhibition of recrystallization by lowering the line energy of dislocations

due to a positive solute excess at dislocations

- reduction of the grain size in a polycrystalline material in order to harden it by grain boundary hardening
- softening of metals by solute atoms at low temperatures
- stabilization of nanocrystalline materials by grain boundary or surface segregation regarding the coarsening at elevated temperatures

4.2.1 The role of H in Pd

H differs from other defactants in metals in several important aspects which have to be kept in mind when discussing the effects of H on lattice defects [69]. Furthermore, H can be understood in metals as a special alloying addition [21]. It can be dissolved in a metal at a higher temperature in order to create changes in the microstructure and removed at lower temperature. Therefore H is sometimes called a "temporary" alloying addition [21]. It also has to be remarked that Pd forms no Pd hydride in the meaning of covalent bonded H as in AlH_3 , TiH_2 or Ta_2H for example [10]. It is common to speak of "palladium hydride" PdH_x when H is dissolved at interstitial sites in the Pd lattice!

H persists in octahedral interstitial sites in Pd [69]. It has a constant, large partial molal volume, i.e. molar volume of a dissolved substance, of $V_H = 2.9 \text{ \AA}^3 = 2.9 \times 10^{-30} m^3$ [69] and hence a large distortion field within a host metal. The interaction of H with dislocations appears to be that of an elastic stress center. Due to a very small activation enthalpy (0.23 eV for H in Pd [69]) and the fact that H is not covalent bonded, the mobility of H and therefore its diffusivity is extremely high. For the same reasons the H mobility is very dependent on trapping at lattice defects which might retard the diffusion of H in Pd noticeable.

The impact of solute H in Pd on deformation-induced lattice defects is manifold. As long as the solute H is able to move with a dislocation, it can increase the dislocation mobility. This can be explained on the basis of a theory of "elastic shielding" which protects the dislocation during interactions with other elastic stress centers [69]. On the other hand, this can also be explained, based on the defactant-concept, by a reduction of the dislocation line energy. Kirchheim reported such a reduction of about 26% [21].

H might also have a contrarious effect on dislocations. Trapped H in a dislocation core can pin the dislocation and therefore decrease the dislocation mobility [69].

Additionally, H promotes the creation of superabundant vacancies by increasing c_{vac} via a reduction of the vacancy formation enthalpy H_v^f [21]. This decrease in H_v^f is then inversely proportional to the chemical potential. Superposed with the rise in c_{vac} is a reduced mobility of these vacancies since the vacancy-H agglomerate has to dissociate before the vacancy can move separately.

Moreover, this mentioned proportionality with the chemical potential is valid for all defects, i.e. grain boundaries, dislocations and vacancies, and therefore lead to enormous increased defect densities by reducing the formation energy of all these defects. Of course H as a defactant in Pd can induce all changes mentioned above, i.e. grain size reduction, stabilization of nanocrystalline materials, enhanced diffusion, inhibition of recrystallization and softening [21]. Especially during sever plastic deformation of Pd-H all these effects occur simultaneously and might counteract one another, i.e. softening by reduction in dislocation line energy and hardening by solute drag or grain refinement.

4.2.2 The role of C in Fe

There are two approaches to interpret the role of solute C in a Fe matrix, both of which are rigorous and valid, however fundamentally different. In the theory of Cottrell clouds of the defects change the site energy for a solute atom [70][71]. In contrast to Cottrell's concept, the defactant concept describes a decrease in the overall free energy by interactions between solutes and defects due to a decrease in the defect formation energy [20][21]. This work will focus on the defactant concept.

C as a defactant in Fe, in comparison to H in Pd, is much less mobile and therefore can be treated as fixed pinning point [68]. Furthermore, the equilibrium solubility of C in Fe is extremely limited at room temperature [72][73]. Nevertheless the concentration of C dissolved in nanocrystalline Fe-C alloys processed by ball milling is found to be much larger than its equilibrium values [73]. Additionally, no significant change in the unit cell volume during plastic deformation can be observed [73][74]. However, a distinct variation of the C concentration can be seen in a Fe-C system indicating a very heterogeneous distribution of C in Fe [75]. A variety of studies confirm a segregation of C atoms in or nearby all kinds of different lattice defects [76][72][73][74]. Especially the segregation of C at grain boundaries may enhance the thermal

stability of nanocrystalline materials via a reduction of the grain boundary energy [73]. Nevertheless one should note that the role of defactants, particularly C in Fe, on the thermal stability of nanocrystalline metals might be rather intricate and is not necessarily linked to segregation of solutes in defects [77].

The interaction of solute C with dislocations is ambivalent. On the one hand is the mobility of C a dislocation-assisted diffusion process, i.e. C atoms can only diffuse within a dislocation core [72][75]. Hence the mechanically driven mass transport of C atoms within the Fe matrix can qualitatively be described by mechanical diffusion parameters [52]. On the other hand, dislocations decorated with C show an essentially reduced mobility, i.e. the dislocation motion is retarded and dislocations are pinned through solute C, respectively [78]. The latter leads to an increased macroscopic strength while the first one results in a transport of C atoms to grain/subgrain boundaries where they segregate. The mutual influence of C atoms and dislocations is a sensitive phenomenon. Slight differences in the local conditions might produce the difference. Not least it is found that the segregation of C to dislocations lowers the line energy of dislocations substantially [79].

The interaction of solute C with vacancies seems to be more straightforward than the C-dislocation interaction. It is well known that C and vacancies form Vac_1C_2 - or/and Vac_2C_4 -clusters, e.g. [54][74][79]. These clusters show a restricted mobility and diffusivity, respectively. The binding energy of vacancy-C-clusters was determined to be 0.75 eV and 0.85 eV by positron lifetime spectroscopy [80][81]. In [80][81] the authors determined the formation energy of vacancies with one attached C atom to be remarkably reduced compared to naked vacancies. Due to this reduced formation energy an increased concentration of undecorated as well as C decorated vacancies can be found [74]. Furthermore, the concentration of vacancies is proportional to the C concentration which implies that the increase in c_{Vac} with increasing C concentration is larger than the concomitant decrease in vacancy diffusivity [74].

Additionally, C can segregate at grain boundaries. It is well known that the formation of nanocrystalline metals obtained by SPD is related directly to the formation and/or evolution of "non-equilibrium" grain boundaries containing a tremendous density of extrinsic dislocations [73][77]. Thus, the nanocrystalline metals possess enhanced free volume and additional local strains [77]. Defactants, namely C in Fe, can reduce the grain boundary energy via segregation as observed in several studies, e.g. [72][73][77]. C segregates up to 1 at% (= 0.2 wt%) at grain boundaries [72]. Moreover, it was found that with increasing C concentration the grain size decreases and the grain boundary area increases, respectively [73]. The segregation of C at grain boundaries

is also an extremely sensitive phenomenon since it affects significantly the mechanical properties or the thermal stability [77].

4.3 Strengthening mechanisms in metals

There exist several mechanisms increasing the strength of a metal, see e.g. [26][55][56]. In the framework of these investigations dislocation hardening, $\Delta\tau_{Dis}$, vacancy loop hardening, $\Delta\tau_{Vac}$, and grain boundary hardening, $\Delta\tau_{GB}$, are of importance. It is noteworthy that mono-vacancies do not strengthen a metal. Not until vacancies have agglomerated into loops they might harden a metal. Therefore the following ansatz can be made

$$\Delta\tau = \tau_0 + \Delta\tau_{Dis} + \Delta\tau_{Vac} + \Delta\tau_{GB} \quad (4.4)$$

where τ is the overall strength and τ_0 is the initial strength of a defect-free single crystal.

The strengthening mechanism based on dislocations can be understood in terms of immobilization of moving dislocations. Here, a dislocation gliding on one plane is interacting with a second converging dislocation of the same type moving on a different plane. Such an interaction of two dislocations may lead to pinned agglomerates, called "Lomer-Cottrell-Locks" [55]. Therefore, these two dislocations affecting each other are immobilized and thus build an obstacle which is impenetrable for following dislocations. Hence, following dislocations encountering the Lomer-Cottrell-Lock are immobilized as well [55]. However, these fixed dislocations contribute to an increase in the internal stress and enhance the agglomeration of further dislocations. Moreover, to allow for an ongoing deformation and the loss of mobile dislocations new dislocations have to be created. This can be achieved by so-called Frank-Read-sources or by emission of dislocations from grain boundaries. The mechanisms increase the strength via strain field of dislocation and the dislocation density. It is therefore reasonable to connect the dislocation density with the strength by the Taylor equation, eq. 4.5, which reflects the arrangement of dislocations [55]

$$\Delta\tau_{Dis} = \alpha G b_{Dis} \sqrt{\rho_{Dis}} \quad (4.5)$$

where α is the dislocation configuration parameter, G denotes the shear modulus, b_{Dis} is the length of the Burgers vector of the dislocation and ρ_{Dis} marks the dislocation density. Table 4.1 lists the values which were used hereinafter for the evaluation of the impact of dislocations on the macroscopic strength.

4.3 Strengthening mechanisms *Theoretical Background*

The length of the Burgers vector of Pd is calculated by $b = \frac{a}{\sqrt{2}}$ (valid for fcc metals)[83] with the lattice constant $a(Pd) = 0.388 \text{ nm}$ [10]. The values for Fe are taken from [79].

material	α	G [GPa]	b_{Dis} [nm]
Pd	0.1 [82]	42.0 [9]	0.2744
Fe	0.40	80	0.25

Table 4.1: Values used hereinafter for evaluation via Taylor equation

There is a smooth transition from dislocation hardening to vacancy loop hardening since dislocation loops are formed either by the condensation of vacancies or by moving dislocations containing large sessile jogs [83]. Therefore, loop hardening can be considered as hardening based on either dislocation loops or vacancy loops. Within this thesis a vacancy loop hardening, where numerous vacancies agglomerate in form of a loop, is employed.

The strengthening mechanism of a vacancy loop arises from the interaction of the loop with moving dislocations, e.g. retards their movement or produce sessile jogs. However, the interaction force of a vacancy loop decreases with l_0^{-3} where l_0 is the distance between the loop and a nearby moving dislocation [83][84]. Therefore, the interaction volume of a vacancy loop is concentrated to the close proximity of the loop. The interaction is rather small if no intersection of the vacancy loop and the moving dislocation occurs. A significant interaction is observed when an intersection takes place. In most cases jogs in the moving dislocation are formed leaving behind a smaller prismatic loop when a vacancy loop and a dislocation with the same Burgers vector intersect [84]. Thus it appears that the interaction energy for given orientations of the loop and the moving dislocations must be a function of their relative positions and the relationship of their Burgers vectors, respectively [83]. Additionally, the dimensions of the vacancy loop must be taken into account. Kroupa et al. derived the following equation to describe the strengthening mechanism by vacancy loop hardening [83][84][85]

$$\Delta\tau_{Vac} = \frac{1}{8}Gb_{loop}(2\pi)^{-\frac{1}{2}}\sqrt{\rho_{loop}\frac{R}{l_0}} \quad (4.6)$$

where G is the shear modulus, b_{loop} denotes the length of the Burgers vector of the vacancy loop, ρ_{loop} is the density of vacancy loops, R marks the radius of the loop and l_0 denotes the average distance between the vacancy loops and a moving dislocation in the same slip plane.

Comparison of eqs. 4.5 and 4.6 shows marked similarities. However, it must

4.3 Strengthening mechanisms *Theoretical Background*

be noted that the Taylor equation, eq. 4.5, is valid for a long-range stress and geometrically extended straight dislocations whereas eq. 4.6 is assumed for a short-range stress of geometrically limited vacancy loops with $l_0 \lesssim 2R$ [84]. Moreover, ρ_{Dis} and ρ_{loop} describe slightly different densities which must be distinguished, i.e. the dislocation density of extended straight dislocations and the vacancy loop density, respectively.

In the framework of this thesis, the density of vacancy loops, ρ_{loop} , was derived from the vacancy density, c_{Vac} , and the length of the Burgers vector of the vacancy loop, b_{loop} , via eq. 4.7 [61] :

$$\rho_{loop} = \frac{4}{\pi} b^2 c_{Vac} \frac{1}{b_{loop}^2} \quad (4.7)$$

where b denotes the length of the Burgers vector in the lattice. b_{loop} was set to 1.1 nm for Pd and Pd-H, respectively, while $b_{loop} = 1.0 \text{ nm}$ was assumed for Fe and Fe-C, respectively.

Another important strengthening mechanisms based on vacancies is hardening arising from vacancies agglomerating into voids which are considered as spherical with radius R_{void} and density n_{void} [84]. For small voids the relaxation of the stress field should be rather small [84]. Like for vacancy loops also for voids the interaction volume is concentrated to the close proximity of the void and therefore no long-range stress must be taken into account. Nevertheless, the interaction energy of the void on moving dislocations is very significant when the moving dislocation is tangential to it or when the dislocation is passing through the void [84]. Analogous to the vacancy loops also for voids the distance between the void and a moving dislocation is crucial for the value of the interaction energy, especially for edge dislocations interacting with a void [84]. Dislocations bypassing the void will undergo a negligible force while the force on the dislocation increases tremendously when intersecting the void and will be a maximum when the dislocation leaves the void [84]. The strengthening via vacancies agglomerated into voids can be expressed according to [84] by

$$\Delta\tau_{void} \propto \frac{1}{10} G b_{Vac} c^{\frac{2}{3}} \left(\frac{4\pi}{3} \right)^{-1} \frac{1}{R_{void}} \quad (4.8)$$

where c is the vacancy concentration, b_{Vac} marks the length of the Burgers vector of a single vacancy, G denotes the shear modulus and R_{void} is the radius of the void. This relation is no more applicable for too large voids.

Comparing the hardness increase of vacancies condensed in a loop or a void

4.3 Strengthening mechanisms *Theoretical Background*

one can find that hardening by vacancy loops is by a factor $\sqrt{\frac{R_{void}}{b}}$ larger than that by voids, assuming a given vacancy concentration and the same concentration of loops and voids [84]. Therefore, with respect to hardness increase by vacancies, it is more beneficial to agglomerate them into loops than into voids.

The strengthening mechanism by grain boundaries arises from the fact that dislocations cannot pass the grain boundaries, mainly because of incoherence of the atomic lattice planes of neighbouring grains. Therefore, moving dislocations are piled-up at grain boundaries. The pile-up stresses in one grain determine the stress to be reached to generate a new dislocation in the neighbouring grain; this model serves to derive the so-called "Hall-Petch equation" which refers the yield strength τ to the grain size d for large angle boundaries (cf. section 4.1.3) as follows [55][56][86][87]

$$\tau = \tau_0 + \frac{K_y}{\sqrt{d}} \quad (4.9)$$

where d is the average grain size, K_y denotes a material-specific constant and τ_0 marks the initial strength of a defect-free single crystal. Moreover, in plastic deformation of metals usually subgrains are formed with so-called "cell boundaries" or "cell walls" which only show accumulation of dislocations in the boundaries/walls which do not cause substantial misorientation between the neighbouring cells/subgrains; they obey another "Hall-Petch-type" equation for small angle boundaries (cf. section 4.1.3) [26][56][88] reading as

$$\tau = \tau_0 + \underbrace{\frac{K_y}{d}}_{\Delta\tau_{GB}} \quad (4.10)$$

and used for eq. 4.11 since only small angle boundaries are expected.

Summarizing the strengthening mechanisms in metals the following equation 4.11 was obtained. The contributions of the different strengthening mechanisms to the overall strength of the two metal-defactant systems can be detected now.

$$\tau = \tau_0 + \alpha G b_{Dis} \sqrt{\rho_{Dis}} + \frac{1}{8} G b_{loop} (2\pi)^{-\frac{1}{2}} \sqrt{\rho_{loop} \frac{R}{l_0}} + \frac{K_y}{d} \quad (4.11)$$

Here τ is the overall strength of the metal, τ_0 marks the initial strength of the

4.3 Strengthening mechanisms *Theoretical Background*

defect-free metal, α as well as K_y are material-specific constants, G denotes the shear modulus, $b_{Dis/loop}$ and $\rho_{Dis/loop}$ are the length of the Burgers vectors and the defect densities, respectively, either of a dislocation or a vacancy loop, R is the radius of a loop and d is the grain size.

In order to investigate the evolution of the macroscopic strength $\Delta\tau$ and τ , respectively, the development of the microhardness ΔHV and HV , respectively, was measured as described in the next chapter. Both are correlated via

$$\Delta\tau = \frac{\Delta HV}{m} \frac{1}{M_\sigma} \quad (4.12)$$

where $m = 3$ is the Tabor factor and $M_\sigma = 3.06$ denotes the Taylor factor for a texture-free face-centered-cubic polycrystal [89] [61].

Chapter 5

Experimental Details

5.1 Preparation techniques

To answer the research questions mentioned in chapter 3 it is necessary to introduce the defactants into the pure metallic matrix and to severely plastically deform the hereby defected samples. The required preparation techniques are described in the following sections.

In the Pd-H system pure Pd provides the matrix metal while H serves as defactant. There are several techniques to charge Pd with H, e.g. Krystian et al. utilized a Sieverts-type apparatus [12][59] while Chen et al. employed an electrochemical approach [13][90]. In this work the electrochemical method for hydrogenation of Pd is used not at least because it is a proved and simple method for hydrogenation.

In contrast, in the Fe-C system the pure Fe conduces to the metallic matrix and C presents the defactant. A very favored method to introduce C into Fe is mechanical alloying via ball milling [19]. This approach results in a nanocrystalline powder which requires a subsequent consolidation. In order to get comparable results in this thesis that technique is also employed.

5.1.1 The process of hydrogenation

A hydrogen formation at a metal electrode can be observed in an aqueous acid solution via a cathodic current. "In statu nascendi", i.e. during the initial period, atomic H is created [90]. These H atoms might either recombine to H_2 molecules or be absorbed by the cathode. However, when the recombination into molecules and the formation of H_2 bubbles are suppressed, H will be absorbed in total by the cathode [90]. This physical principle is used for the process of hydrogenation of Pd via electrolytic charging. The amount of H in the Pd can be calculated by Faraday's Law, eq. 5.1, assuming there is no

other redox system in the electrolyte and the electrode does not corrode [90]

$$\frac{H}{Pd}[\text{at}\%] = \frac{t I}{F} \cdot \frac{M_{Pd}}{m_{Pd}}. \quad (5.1)$$

Here $\frac{H}{Pd}$ marks the H concentration in Pd, t is the time, I denotes the current, $F = 96485 \frac{As}{mol}$ is the Faraday constant, M_{Pd} marks the molecular weight of Pd (cf. table 1.1) and m_{Pd} denotes the sample mass. In this thesis a viscous electrolyte consisting of 1/3 phosphoric acid (H_3PO_4) in 2/3 glycerin ($C_3H_8O_3$) each with a concentration of 85% was employed, see also [13]. The Pd sample was supplied as cathode while vis-à-vis a platinum mesh operated as anode. The electrolysis took place in a conventional 250 ml beaker. To get a stable current output over long time a Model 262 Calibrator/Source by Keithley Instrumernts Inc. was used as DC current source. A constant current with a current density $\vec{j} < 20 A/m^2$ was chosen. Substantial surpassing of this value leads to a large H production rate resulting in partially buoyancy of H instead of adsorption which yields to undefined charging conditions. Coordinated time and current were selected according to Faraday's law, eq. 5.1 for chosen H concentrations. Fig. 5.1 depicts a sketch of the function of the utilized electrolysis for the hydrogenation. It is

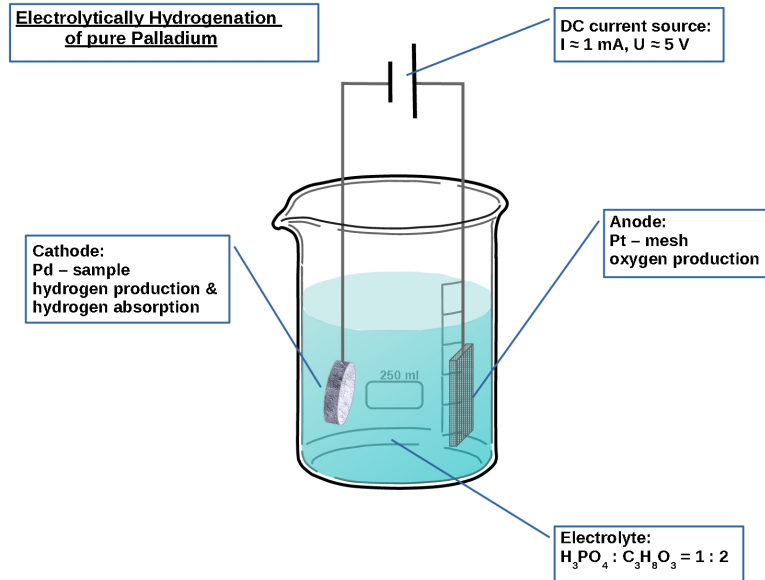


Figure 5.1: sketch of electrolytically hydrogenation of Pd

possible to determine the H concentration by weighing [90] but this was not followed in this work.

After deformation of the Pd-H samples and before the proximate measurements, the H was removed. The electrolytic charging process is reversible and, hence, can be used for removing the H [90]. A second, more simple, method to remove the dissolved interstitial H is to store the hydrogenated sample at room temperature for more than two weeks. This treatment was done in this thesis.

5.1.2 The method of mechanical alloying

The method of mechanical alloying consists of two techniques, (i) ball milling of dissimilar powders up to particles (often nano- or sometimes microscaled ones) with nanocrystals and (ii) a subsequent consolidation of the obtained alloyed powder [26].

Ball milling has been shown to be capable of grain refinement down to the nanoscale of practically all seen elements [26][91]. In this procedure the minimum achieved grain size depends on a variety of process and material parameters. Additionally, the minimum grain size obtained by ball milling has been referred to the dynamic balance between the creation of deformation-induced lattice defects and recovery/annihilation due to thermally activated processes [26]. Moreover, an inverse dependence of the minimum grain size and the melting temperature at least for lower melting metals was reported. Grain sizes below 10 nm for metals with higher melting point were achieved [26]. However, for applications a nanocrystalline bulk material is needed which requests a subsequent consolidation of the ball milled powder alloy. This consolidation is still a challenge, i.e. the ability to keep the nanoscaled grain sizes in the as-milled material and achieve artifact-free bulk samples within minimal grain growth [26]. In that way produced nanocrystalline metals may suffer from the lack of complete bonding due to incomplete powder consolidation.

A large variety of construction principles exist for ball mills, e.g. vibration mills, stirred ball mills, etc. [91]. The type of the ball mill used in this thesis is a planetary mono mill. Fig. 5.2 depicts the fundamental principles of such a planetary mill. The mill material is placed together with balls inside a vial which performs a rotary motion around the mill axis with an angular velocity Ω and a planetary motion around the vial axis with an angular velocity ω [91][92]. Planetary mills practice the principle of centrifugal acceleration by combination of two centrifugal fields. The process parameters in ball milling are the following and might have an enormous influence on the milling result [91].

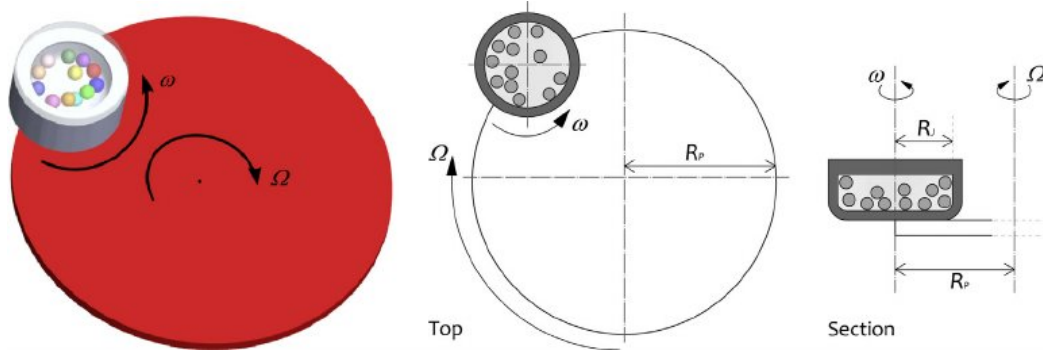


Figure 5.2: the functional principle of ball milling [92]

- the milling time
- the ball to powder ratio
- the temperature of the balls and of the mill material
- air, vacuum or protective gas atmosphere in the vial
- the material of the milling balls

A serious problem in ball milling is contamination due to the small size of milled particles and the formation of new surfaces during milling. Possible sources for contaminants are the atmosphere in the vial and abrasion of the milling balls. The application of shortest milling times, a protective atmosphere and balls from (or coated with) the same material as the mill charge, may reduce contamination during ball milling [91].

Producing bulk materials out of ball milled powders needs efficient methods of consolidation. The requirements of such methods are densification of the powder up to closely 100 % of the theoretical density and sufficient size and shape of the sample [26]. The parameters of the consolidation method are restricted to suppress grain growth, precipitation of phases and crystallization of amorphous phases. Moreover, aggregation of particles and high interparticle forces are problems associated with the densification of powders of nanosized particles [26]. A high pressure of several GPa assists the densification [26]. HPT, for example, can provide these conditions.

Hence, the final microstructure of a mechanically alloyed material depends not only on the ball milling parameters, but also on the characteristics of the consolidation procedure.

5.1.3 High Pressure Torsion

High Pressure Torsion (HPT) is a suitable method to receive severe plastic deformation with degrees of deformation $\gamma \gg 5$. This method possesses three main advantages over all other SPD techniques. These are, (i) extremely large plastic deformation by simple shear straining (ii) continuous without interruption or changes in the strain path and (iii) a well controlled and enhanced hydrostatic pressure [12][94]. The latter reduces the diffusion within the solid and therefore delays the recovery kinetics of lattice defects [51]. Moreover, a higher applied pressure facilitates grain refinement during deformation and thus the strength of the metal via the Hall-Petch mechanism (cf. eq. 4.9) [51].

Fig. 5.3(b) provides a photograph of the used HPT machine while fig. 5.3(a) sketches the functional principle of HPT. A disc-shaped specimen is placed within cylindrical cavities of two anvils. After applying the pressure one of the anvils is rotated in order to achieve plastic torsional straining [59][94]. The initial diameter of the HPT sample and the diameter of the cylindrical cavities have to be almost identical. While the high pressure of several GPa is established, a small amount of material flows in the ring shaped region between the two anvils creating a back pressure which introduces a hydrostatic pressure within the processing zone [94]. The main purpose of the hydrostatic pressure is the suppression of fracture, i.e. initiation, growth and propagation of cracks [51]. Due to such high hydrostatic pressures, a com-

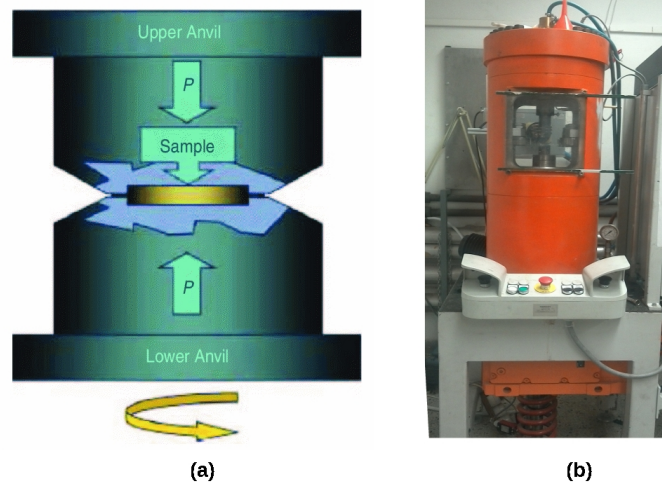


Figure 5.3: High Pressure Torsion: (a) sketch of function principle [95] (b) photograph of HPT machine used

pressive plastic shear is left which should be kept below $\frac{d - d_0}{d_0} = 0.1$ with d_0 and d denoting the thickness of the sample before and after compression, respectively [59]. However, such a compressive strain is usually negligible in relation to the applied torsional strain, except in the center of the sample [94].

In order to clean the cavities of the anvils and to provide the micro-roughness needed for sufficient friction for a continuous torsional deformation, the bottom and the top face of the cylindrical cavities of the anvils have to be sandblasted [94]. Even then the necessary pressure to avoid sliding between the sample and the anvils, has to be usually very high. As a rule of thumb, the pressure should be larger than the hardness of the material [94]. However, the maximum applicable pressure in a HPT equipment is limited by the hardness of the anvil material.

A HPT-specific feature is the heterogeneity in the microstructure, and thus in the properties of the sample, between center and edge of the sample at small torsional strains. In detail, the true torsional strain γ is given by [59][94]

$$\gamma = \frac{\phi r}{d} = \frac{2\pi n r}{d} \quad (5.2)$$

where r and d are the distance from the axis of rotation and the thickness of the sample, respectively, $\phi = 2\pi n$ denotes the torsional angle in radians and n marks the number of turns. However, the increases with increasing straining [49] end for torsional strains $\gamma \gtrsim 15$ in most single phase materials. When a saturation value is reached a homogeneous microstructure can be observed [94].

For comparison of straining via HPT with that created by cold rolling the true equivalent strain, defined by $\epsilon = \frac{\gamma}{a}$, is helpful. Here the coefficient a takes either the value from plastic flow criterion, i.e. $a = \sqrt{3}$ for von-Mises or $a = 2$ for Tresca, or from the Taylor theory for polycrystals with $a = 1.65$ (texture free fcc metal) [59]. In the framework of this thesis a von-Mises equivalent strain, ϵ_{vM} , for HPT calculated via eq. 5.3 is used.

$$\epsilon_{vM} = \frac{1}{\sqrt{3}} \frac{2\pi n r}{d} \quad (5.3)$$

Walter Klement GmbH, type HPT02, manufactured 2009, with a 150 tons maximum press capacity was used as HPT facility.

5.1.4 Cold Rolling

Rolling is a well established technique and applicable to get medium plastic deformations with degrees of deformation $\gamma \lesssim 5$. Rolling can be classified with respect to the recrystallization temperature T_{rec} in cold rolling at $T_{roll} < T_{rec}$ and hot rolling at $T_{roll} > T_{rec}$, respectively [93]. Fig. 5.4 sketches the functional principle of cold rolling. A sheet of a coarse-grained metal with initial thickness d_0 is introduced between rollers and therein thinned to an end thickness d . Simultaneously the sheet is lengthened due to volume conservation [55] and a grain refinement occurs. Additionally, the grains get aligned and evolve in a preferred crystallographic orientation parallel to the rolling direction [56][55]. The most important fact, in the framework of this thesis, is that during cold rolling various deformation-induced lattice defects are created in the metal sample. Furthermore, cold rolling results always in a specific texture [55][56]. The corresponding von-Mises true equivalent strain, ϵ_{vM} , achieved in cold rolling is given by eq. 5.4 where d_0 and d denote the initial and end thickness, respectively.

$$\epsilon_{vM} = \ln \left(\frac{d_0}{d} \right) \quad (5.4)$$

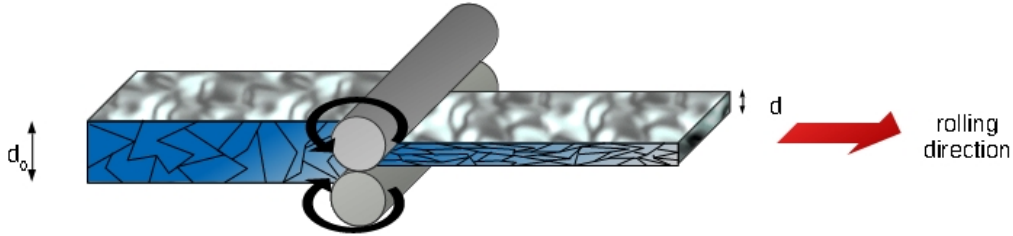


Figure 5.4: functional principle of cold rolling

5.2 Sample preparation

To answer the first block of questions, it was necessary to prepare several samples of Pd-H. To investigate the effect of H on deformation-induced lattice defects and the importance of the H concentration in Pd, H/Pd, Pd samples were prepared with significantly different H/Pd values. Furthermore, large as well as medium degrees of plastic deformation were chosen in order to study the effect of deformation strain γ on the nature and density of defects.

Moreover, the influence of processing temperature of SPD deformation was of interest. Thus, samples processed by HPT at two processing temperatures, and by cold rolling were prepared.

For the investigations on the Fe-C system, only one concentration of C, i.e. 0.8wt% C, was chosen. Fe and C were mechanically alloyed, consolidated and severely plastically deformed. SPD by HPT allowed to unify these two treatments in one step, by means of the same processing temperature. By varying the pressure as well as the number of rotations, it was possible to check the influence of these parameters on the densities of lattice defects.

5.2.1 Pd-H

In order to obtain a first set of samples of Pd-H, a commercial Pd sheet with a purity of 99.95% (by Wieland Edelmetall GmbH) was punched into disks of 8 mm diameter and 0.5 mm thickness via spark erosion (Charmilles Isopulse Type P25). The Pd disks were cleaned by sandblasting and annealed at 800°C for 2h in a resistance furnace (Heraeus Typ Ro 4/25) at an ultra high vacuum. Afterwards these samples were electrically contacted using conductive silver and a thin film of glue (UHU hart) protected the contacts against the electrolyte during the following hydrogenation process. The above described electrolytic charging procedure was used to hydrogenate the samples with H concentration of H/Pd = 0.0025, 0.0075, 0.20 and 0.45, respectively. Therefore, corresponding currents of $I = 0.2, 0.3, 5.0$ and 6.0 mA, respectively, and loading times, t , ranging from 58 min up to 349 min were applied. All electrical contacts were released via acetone. The achieved H/Pd ratios were calculated using Faraday's law (eq. 5.1) and checked via weighing before and after hydrogenation. Several samples of each H concentration were prepared.

Subsequently the samples were severely plastically deformed using a HPT facility with a hydrostatic pressure of 8 GPa, at a speed of 0.2 rpm and for 4 rotations according to a maximum, i.e. at the edge of the sample, torsional strain of $\gamma = 201$ and a maximum von-Mises equivalent strain $\epsilon_{vM} = 116$, respectively. One half of the set of samples were processed in the HPT machine at room temperature while the the second half of samples were processed via HPT at a temperature of 194 K = -79°C using solid CO_2 pellets for cooling the anvils, named in the following "CO2". Before the following measurements the H was removed by storage at RT for at least 4 weeks. The disappearance of dissolved H was detected by weighing and showed no significant changes anymore after already 2 weeks.

Additionally, a reference sample was prepared by performing all above described preparation steps identically except the hydrogenation which was

omitted. Thus, the impact of H on the deformation-induced lattice defects could be studied. Table 5.1 is summarizing the relevant preparation data.

sample identifier	H/Pd	I [mA]	t [min]	T_{HPT} [K]	p_{HPT} [GPa]	number rotations	ω_{HPT} [rpm]	mass [mg]
#1	0.45	6.0	349	296	8	4	0.2	307.98
#2	0.45	6.0	347	194	8	4	0.2	306.60
#3	0.20	5.0	186	296	8	4	0.2	308.27
#4	0.20	5.0	185	194	8	4	0.2	306.77
#5	0.0075	0.3	117	296	8	4	0.2	308.30
#7	0.0025	0.2	59	296	8	4	0.2	308.08
#9	0.0075	0.3	116	194	8	4	0.2	307.20
#10	0.0025	0.2	58	194	8	4	0.2	306.55
#11	without	-	-	296	8	4	0.2	307.35

Table 5.1: The relevant preparation data for HPT-processed Pd-H

A second set of samples of Pd-H was obtained by cutting the same Pd sheet mentioned above into platelets $5 \times 5 \times 0.5 \text{ mm}^3$ in size using spark erosion. The Pd plates were sandblasted for cleaning and annealed at 863 K for 2 h in a DSC (Netzsch DSC 204) under an argon atmosphere. The electrical contacting was performed using electric paint (Bare Conductive) and a thin film of epoxy resin as protection. Electrolytic hydrogenation was conducted up to H concentrations of 0.0075, 0.45 and "without H" (as reference), respectively. This was reached by charging with 0.3 mA for 55 min ($\text{H/Pd} = 0.0075$) and with 2 mA for 441 min ($\text{H/Pd} = 0.45$), respectively. Acetone was used for releasing the electrical contacts. Weighing was performed to check the achieved H/Pd ratios and Faraday's law (eq. 5.1) was employed for its calculation.

The samples were subsequently plastically deformed via cold rolling to about $d = 0.5 d_0$ with the initial thickness d_0 using a commercial plate roll with two rolls operating at a rolling width of 20 cm. Since the results of the HPT-processed samples indicated no significant influence of the deformation temperature, only one temperature of cold rolling was chosen, i.e. $T_{CR} = 296 \text{ K}$. As done also before, the H was removed before the proximate measurements via storage at RT for at least 2 weeks and the disappearance of dissolved interstitial H was determined by means of weighing. The following table 5.2 is visualizing the suitable preparation data.

sample identifier	H/Pd	I [mA]	t [min]	passes	d_0 [mm]	$\bar{d}$ [mm]	ϵ_{vM} acc. to eq. 5.4	mass [mg]
#1	without	-	-	1	0.51	0.23	0.80	128.89
#2	0.0075	0.3	55	1	0.54	0.26	0.73	148.91
#3	0.45	2.0	441	1	0.53	0.25	0.75	128.55

Table 5.2: The suitable preparation data for CR-deformed Pd-H

Storage and transportation of all hydrogenated samples took place under liquid nitrogen to avoid uncontrolled H losses.

5.2.2 Fe-C

Samples of nanocrystalline Fe0.8wt%C were obtained by mechanical alloying of Fe powder with 99.99% purity and 0.8 wt% graphite flakes with a purity of 99.99%. Therefore the powders were sealed in a 250 ml tempered steel vial with stainless steel balls in an argon atmosphere. The ball to powder mass ratio was chosen to be 10:1. In order to avoid oxidation, the powders were handled in a glove box with argon atmosphere. Ball milling was conducted for 100 h at room temperature at a speed of 250 rpm using a planetary ball mill (Fritsch Pulverisette 6 classic line). Additionally, a nanocrystalline reference material of pure Fe was processed by ball milling using the identical parameters.

For the following consolidation Cu rings with a thickness of 0.7 mm and an inner diameter of 8 mm were cut out of a commercial Cu tube via spark erosion. These rings were used as dies during the consolidation, i.e. the ring was placed in the cavity of an anvil, filled with nanocrystalline powder and subsequently pressed with high pressure using a HPT facility. Immediately after the consolidation, the powders were severely plastically deformed via HPT. For Fe-C three different numbers of rotations, i.e. 4, 10 and 20 rotations, and for pure Fe, two different numbers of rotations, i.e. 4 and 10, were chosen. Thus, three different maximum torsional strains for Fe-C were obtained, i.e. $\gamma = 144$, $\gamma = 359$ and $\gamma = 717$, respectively, corresponding to three different von-Mises equivalent strains $\epsilon_{vM} = 83$, $\epsilon_{vM} = 207$ and $\epsilon_{vM} = 414$. For pure Fe the first two γ and ϵ_{vM} , respectively, were obtained. Moreover, two different pressure values during consolidation and deformation were selected, i.e. 4 and 6 GPa. Consolidation as well as deformation were carried out at room temperature. The densities of the obtained samples were measured using the buoyancy method according to Archimedes, i.e. the masses of the samples were determined with a hydrostatic balance, in distilled water and

in air, and the density of the sample was determined and the density of the sample evaluated in relation to the density of the water.

Assuming a theoretical bulk density of 7900 kg/m^3 for Fe0.8wt%C (cf. table 1.2) and of 7860 kg/m^3 for pure Fe, respectively, the densification was calculated. Densifications of up to more than 99% could be reached. Table 5.3 is summarizing the relevant preparation data of samples of Fe-C. It should be mentioned that a consolidation of pure Fe powder was not possible at a pressure of 4 GPa. All obtained samples were too fragile to take them out of the anvils and thus were destroyed.

All ball milled powders were prepared and supplied by the group of Prof. Y.Z. Chen, Northwestern Polytechnical University, Xi'an, PR China.

sample identifier	C content [wt%]	p_{HPT} [GPa]	number rotations	mass [mg]	density [kg/m^3]	densification
FeC_10rot_3.8GPa	0.8	4	10	334.199	7540	> 95 %
FeC_20rot_4GPa	0.8	4	20	387.338	7420	> 93 %
FeC_4rot_6GPa	0.8	6	4	364.871	7860	> 99 %
Fe_10rot_6GPa	without	6	10	311.683	7160	91 %
Fe_4rot_6GPa	without	6	4	481.248	7470	95 %

Table 5.3: The relevant preparation data for Fe0.8wt%C

5.3 Measurement techniques

In order to analyze the strengthening mechanisms in metals enriched with defectants as mentioned in the introduction and it was necessary to measure the influence of the different deformation-induced lattice defects separately. An appropriate method to do this is to measure the properties of the samples in an isochrone. Relevant quantities to be investigated are the microhardness, the crystallite size and grain size, respectively, the dislocation density and the vacancy concentration.

The microhardness is a suitable quantity to study the strengthening of metals since it is in most cases proportional to the macroscopic strength (i.e. ultimate tensile strength) and can be repeatedly measured with the same sample. DSC, in turn, is an easy and fast technique to detect the defect concentrations and to identify the type of deformation-induced lattice defect via a measurement of their annealing temperature and activation (i.e. migration) enthalpy [59]. In addition, XLPa is another important method

to characterize deformation-induced lattice defects i.e. dislocations and the crystallite (coherent scattering domain) sizes, i.e. the size of the largest possible crystalline area with no crystal defect within it [59].

None of these methods is solely capable to fully identify the defects and their specific impacts on the macroscopic strength so that the combination of these methods makes sense. In the following sections, these methods are described in close details.

5.3.1 Microhardness

As already mentioned, is one of the few mechanical test methods which are fairly non-destructive. Here, with a defined test load, an indenter is pressed perpendicularly onto the surface of a specimen. The test load F over the contact area of the residual indent A is defined as hardness $H = \frac{F}{A_{contact}}$. In conventional hardness measurements the contact area $A_{contact}$ is usually evaluated from the dimensions of the projected area. Hardness measurements with a test load F in the range $100mN < F < 2N$ are called *microhardness* measurements according to ISO 6507-1. Furthermore, mostly a diamond indenter in the form of a square based pyramid and with an angle of 136° between opposite faces at the vertex is referred to as a Vickers indenter (see Fig. 5.5 (a)). Such a Vickers indenter leads to a squared indentation whose projected area is determined by measuring the length of its two diagonals d_1 and d_2 (in μm). The microhardness HV (in $MPa = N mm^{-2}$) is then calculated via eq. 5.5.

$$HV = \underbrace{\frac{2 \sin\left(\frac{136^\circ}{2}\right)}{\left(\frac{d_1+d_2}{2}\right)^2}}_{1/A_{contact}} F = 1.8544 \frac{F}{\left(\frac{d_1+d_2}{2}\right)^2} \quad [MPa] \quad (5.5)$$

In the framework of this thesis an Anton Paar MHT4 microhardness tester equipped with a Vickers indenter and mounted on a Zeiss Axioplan optical microscope equipped with an AxioCam MRc 5 digital color camera was used. The digital images of the indents were analyzed using the software AxioVs40 V4.8.2.0 provided by Carl Zeiss GmbH. Fig. 5.5 (b) provides a photograph of this equipment with the inset showing the measuring head of the MHT 4 fixed on the nosepiece. All samples were wet ground before the microhardness measurements. Further, all measurements took place at room temperature. In addition, the test load F was chosen so that the indents had a minimum size around $30 \mu m$ to minimize the measurement uncertainty.

The test load was held for a duration of 10 s in all measurements. Moreover, every hardness value is the arithmetic mean of at least 10 indents from at least two different locations on the sample in order to get good statistics. These two different locations were in the same distance from the center for the disk-shaped HPT-processed samples to ensure the same hardness value and a good accuracy. The distance between adjacent indents was at least 3 times the length of the diagonal to avoid a mutual influence as recommended in ISO 6507-1. Since a rule of thumb, according to ISO 6507-1, requests a sample thickness of more than 1.5 times the length of the diagonal, i.e. $\sim 30\mu\text{m}$, the cold rolled samples with a thickness of $\sim 250\mu\text{m}$ (cf. table 5.2) were ground and measured with great care.

5.3.2 Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) is a destructive measurement in the sense that lattice defects are annealed. Nevertheless, DSC is a powerful tool since it can distinguish defects with different activation (i.e. migration-) enthalpies [59] e.g. vacancies and dislocations being important in the current work. Broadly DSC detects the energy of transformation processes. The measurement principle of a power compensated DSC is to record the necessary energy to achieve a zero temperature difference between a reference material and a substance against either temperature or time [59]. During the

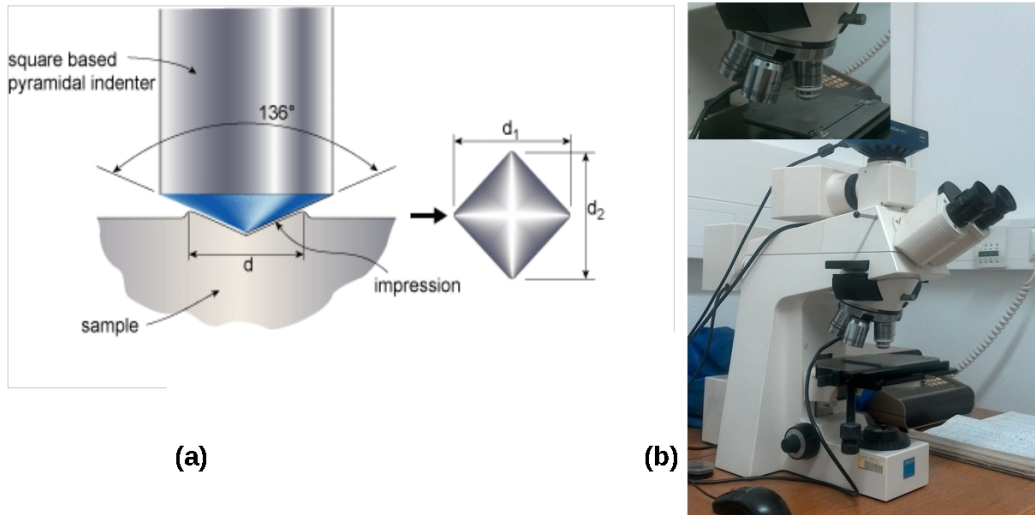


Figure 5.5: Microhardness: (a) principle of measurement with Vickers indenter [96] (b) photograph of the optical microscope with the indenter attached

measurement in DSC, a sample is heated over a range of temperature with a constant heating rate. At some point an absorption or a release of heat can be observed due to chemical or physical changes, e.g. - for the latter - the annealing of deformation-induced lattice defects. Integrating the area under the heat flow curve results in the enthalpy change correlated to the physical change of interest [59]. DSC might investigate a large variety of observable processes, however in the framework of this thesis the changes in the heat flux due to the annealing of deformation-induced lattice defects are of special interest. Fig. 5.6 (a) sketches this described measurement principle and shows additionally the constant heating rate and the resulting DSC plot with endothermic and exothermic peaks. The annealing of deformation-induced lattice defects results in exothermic peaks and can therefore rather easily be distinguished from phase transitions which show endothermic peaks. The analysis of different defect types is possible based on the homologous temperature at which an exothermic peak is observed since every defect type has its characteristic homologous temperature to be annealed. This was demonstrated in [12], [57], [59] or [46], to mention only a few of them. Moreover, the concentration of the deformation-induced lattice defects can be evaluated directly for each defect type from the area of the annealing peak. Dislocations have the highest activation enthalpy of all lattice defects considered in the framework of this thesis and, therefore, anneal at the highest temperature [12][46][59]. The dislocation density ρ can be evaluated via eq. 5.6

$$E_{stor} = Gb^2 \frac{\rho}{4\pi\kappa} \ln \left(\frac{1}{b\sqrt{\rho}} \right) \quad (5.6)$$

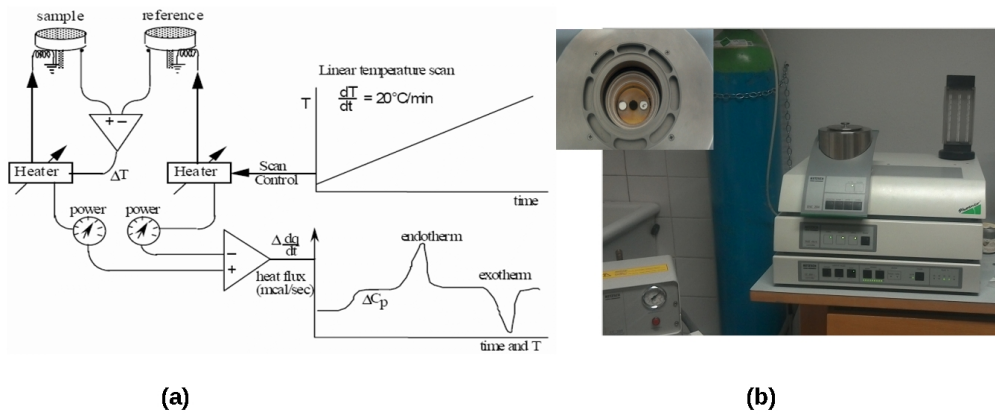


Figure 5.6: Differential Scanning Calorimetry: (a) sketch of the functional principle [59] (b) photo of equipment

where E_{stor} is the stored energy of dislocations, G denotes the shear modulus, b is the absolute value of the Burgers vector, $\kappa = \frac{1 + (1 - \nu)}{2}$ marks the proportion of pure edge "1" and pure screw " $1 - \nu$ " dislocations [68], respectively, which is assumed to be the arithmetic average for equal parts of them with ν the Poisson ratio [59]. In eq. 5.6 it is implied that the external cut-off radius and the distance between the dislocations are equal. This is not necessarily true for all conceivable dislocation configurations [59].

In the framework of this thesis, single vacancies have the lowest activation enthalpy of all lattice defects and thus the lowest annealing temperature [12][59]. The concentration of single vacancies, c_{Vac} , can be evaluated via eq. 5.7

$$c_{Vac} = \frac{E_{Vac}}{\Delta H_v^f} \cdot \frac{M}{N_A} \quad (5.7)$$

where E_{Vac} presents the stored energy of mono-vacancies, ΔH_v^f denotes the formation energy of a single vacancy, M marks the molar mass and N_A is the Avogadro constant.

vacancy-agglomerates forming, for instance, voids have a homologous temperature to anneal in between that of single vacancies and that of dislocations due to a mutual thermal stabilization of vacancies [12][57][59][46]. Eq. 5.7 is also applicable for vacancy-agglomerates resulting in the concentration of single vacancies assembled in larger clusters.

All DSC measurements were performed using a Netzsch DSC 204 equipped with liquid nitrogen for cooling purposes and argon for protective gas atmospheres. Fig. 5.6 (b) shows a photograph of this equipment. The inset provides a view in the measuring chamber of the used DSC device with two Al or Pt pans on top of the two furnaces. The evaluation of the DSC plots was done by employing the software "Netzsch Proteus - Thermal Analysis - Version 4.8.1". The minimum peak area to be measured was 0.05 J/g corresponding to a resolution limit of a minimum vacancy concentration of $c_{Vac} > 3 \times 10^{-5}$ and a minimum dislocation density of $\rho > 3 \times 10^{14} m^{-2}$, respectively [59]. To check carefully the annealing of defects, each measurement consisted of two heating/cooling cycles. Phase transformations would be detectable in every cycle while the annealing of defects only occurs in the first heating/cooling cycle. A more significant feature is that phase transformations always appear as endotherm peaks whereas those of defect annealing achieve exotherm ones.

5.3.3 X-Ray Diffraction and X-Ray Line Profile Analysis (XLPA)

As noticed before, X-Ray Diffraction (XRD) is the experiment of obtaining a X-ray diffraction pattern while X-Ray Line Profile Analysis (XLPA) is the method for analyzing the recorded XRD Bragg peaks themselves (mainly their broadening). XLPA is a non-destructive technique and sensitive to dislocations and very small sizes of the crystallite size. Although a grain itself is limited by high angle boundaries its interior is often divided by small angle boundaries into subgrains which are referred to as "crystallite" or "cell", respectively. Such crystallites represent the largest possible crystalline area without any disturbance within it [59]. The crystallite size is not necessarily the same as the grain size. However, for nanoscaled grains the grain size is only a few times the crystallite size and, thus, it is an appropriate measure for the grain size. To indicate this small difference and to use correct terms GB, i.e. grain boundary, will be replaced with SB, i.e. subgrain boundary, whenever it seems necessary.

The principle of XRD is based on interference of monochromatic X-rays which are elastically scattered from a crystalline sample (see Fig. 5.7 (a)(b)). X-rays are created via an X-ray tube, filtered to monochromatic radiation, collimated and focused on a sample [97]. The X-rays interact with electrons present in the atoms and are scattered there. A diffraction pattern of the sample is obtained by constructive and negative interference and recorded via the detector. Peak positions, i.e. the scattering angle 2θ of the peaks, can be calculated via Bragg's law. XRD was performed using a highly monochromatic X-ray beam in the home laboratory utilizing a RIGAKU MultiMax 9 rotating anode generator (target material Cu) with a Ge single crystal

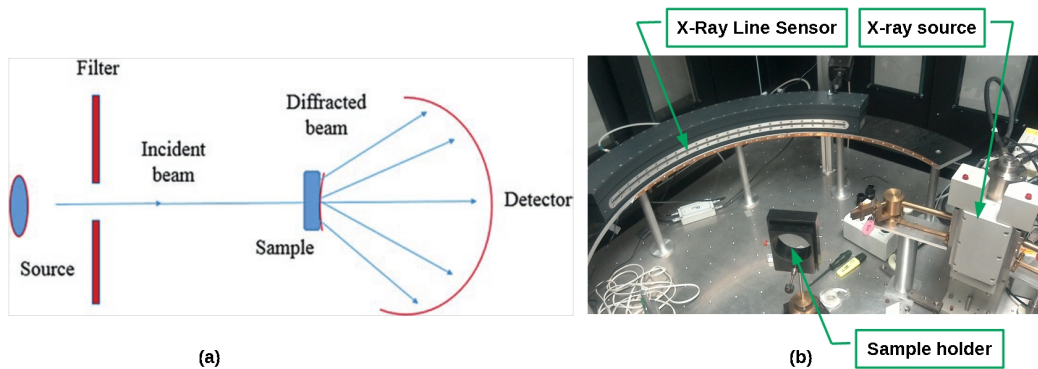


Figure 5.7: X-Ray Diffraction: (a) functional principle [97] (b) photograph of the used equipment

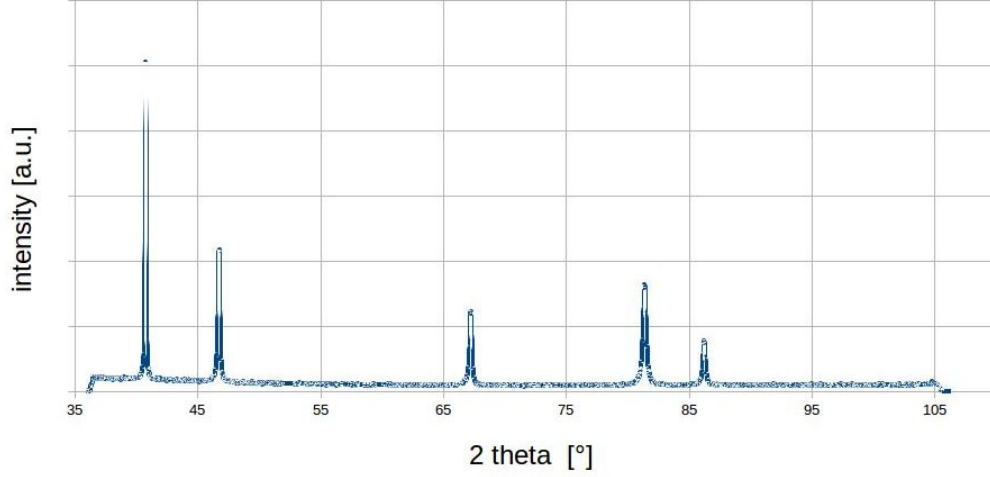


Figure 5.8: Typical XRD pattern of HPT-processed Pd-H with $H/Pd = 0.0025$ and $T_{deform} = -79^\circ C$

monochromator. The employed Co K_{α_1} radiation with $\lambda = 0.179 \text{ nm}$ was monochromatic with $\delta\lambda/\lambda < 10^{-4}$. The spot size on the sample was about $100 \times 500 \mu m^2$. The Bragg reflections were recorded via an Inel CPS-590 linear position sensitive detector which covers an angular range of 90° at a radius of 500 mm. Fig. 5.7 (b) provides a photograph of this equipment used.

Fig. 5.8 shows an XRD pattern of HPT-processed Pd-H ($H/Pd = 0.0025$, $T_{deform} = -79^\circ C$) as an example of a typical diffraction pattern obtained via XRD. As already mentioned, the task of XLPA is to quantitatively analyze the width and shape of the Bragg peaks (beside its general shift), which provide information on crystallite size and size distribution, as well as the density and the arrangement of dislocations. In a conventional Williamson-Hall Plot the peak width $\Delta K = \frac{2\cos\theta}{\lambda}\Delta\theta$ is plotted against the peak position $K = \frac{2\sin\theta}{\lambda}$, where λ is the used wavelength and θ is the scattering angle [62]. This plot in general shows no monotonous behavior. By introducing the dislocation contrast factor $C_{hkl} = C_{h00} \left(1 - q \frac{h^2k^2 + h^2l^2 + k^2l^2}{h^2 + k^2 + l^2} \right)$ where h, k, l are the Miller indices and q is a parameter indicating the fraction of screw and edge dislocations, a monotonous behavior results. This modified Williamson-Hall Plot is achieved by plotting the peak width ΔK as function of $K\sqrt{C}$ [63][64]. In case of the presence of dislocations, this graph is mostly

a linear function with its slope proportional to the dislocation density ρ , and with an intercept, $\alpha K - O$, which represents the crystallite size.

A reliable XLPA can be done when fitting the whole profile. This is realized by a least-squares based approach in the open source software (C)MWP-fit [65][98]. (C)MWP-fit fits the whole measured diffraction pattern by the sum of ab-initio theoretical functions for strain and size broadening, respectively, and a background function [98]. Furthermore, the software assumes a lognormal size distribution of the crystallites and a strain induced solely by dislocations. The dislocation contrast factor C_{hkl} and an ellipticity of crystallites is considered in order to take strain and size anisotropy into account [98]. Based on the selected crystal system, the lattice constant, the absolute value of the Burgers vector, a dislocation contrast factor C_{h00} and the employed wavelength, the software can provide not only the dislocation density, ρ , but also a measure for the intensity of the strain field caused by their arrangement, $Re/\sqrt{\rho}$, the dislocation contrast by qC_{hkl} as well as the median and the variance of the crystallite size distribution and the ellipticity of the crystallites via fitting the whole XRD pattern [98].

The results of these fittings are considered as (i) the area weighted average crystallite size, D , and (ii) the dislocation density, ρ (see [66][67])

5.3.4 Isochronal Annealing

Isochronal annealing is a well established method and - with respect to separation and characterization of lattice defects - a very suitable technique. By evaluating the height of annealing steps, it can inform on the density/concentration of lattice defects, but can be also combined with materials properties such as hardness and/or structural parameters like crystallite size, a description can be found elsewhere, e.g. in [45]. Fig. 5.9 sketches such an isochrone. Since every type of lattice defect has a distinguished activation/migration enthalpy and therefore a characteristic homologous temperature to be annealed, the defect concentration of every lattice defect (or the physical property connected) shows a drastic change (decrease or sometimes increase) at a specific temperature. As can be seen in fig. 5.9, interstitials and interstitial clusters (which e.g. are formed when the materials contains more impurities/alloy atoms) anneal in annealing stages I and II at a temperature around $0.1T_m$ and $0.2T_m$, respectively [44]. In annealing stage III at $T \approx 0.25T_m$ single- and double-vacancies are annealed. Vacancy clusters are thermodynamically more stable than single vacancies and thus anneal at a slightly higher temperature in annealing stage IV. At last, dislocation-type defects anneal in stage V at $T \approx 0.4T_m$ [44]. An isochrone can be derived

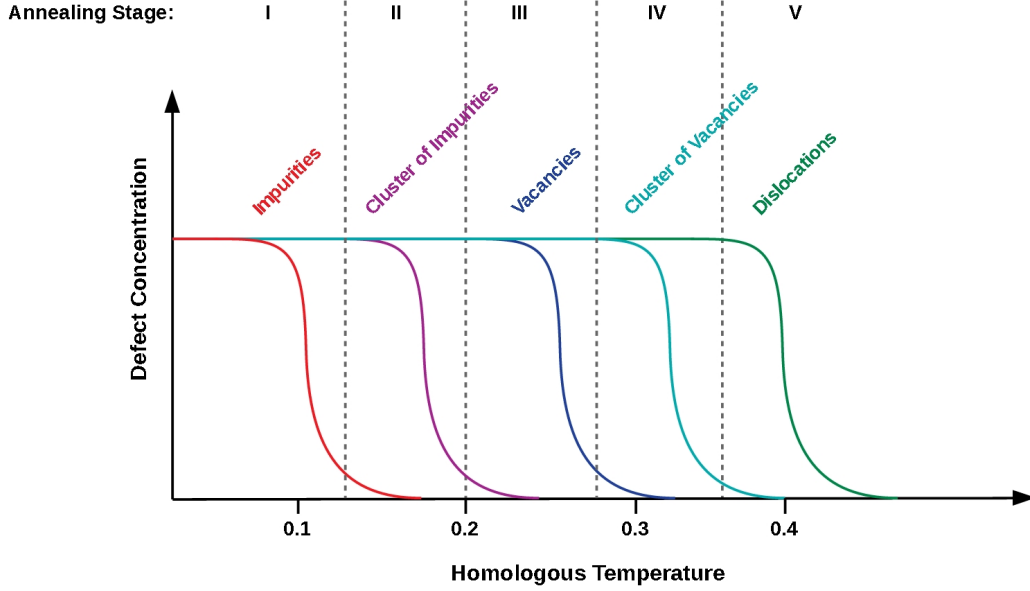


Figure 5.9: Principle of an isochrone in order to separate lattice defects

either by a collection of several isotherms - each annealed at one specific temperature - or by a successive heat treatment of always the same sample. In the framework of this thesis the latter procedure was applied, because only this type of isochrones can be compared with the results from DSC performed with a constant heating rate.

In the current work, the samples were annealed by using either a temperature controlled oil bath (Haake S F3 Fisons) at $T \leq 200^\circ\text{C}$, the furnaces in a DSC under argon atmosphere (Netzsch DSC 204) at $200^\circ\text{C} < T \leq 590^\circ\text{C}$ or a vacuum furnace (Heraeus Typ Ro 4/25) at $T > 590^\circ\text{C}$ in an ultra high vacuum. The isochronal annealing temperatures were chosen so that $0.15T_m < T \lesssim 0.5T_m$ in order to investigate vacancies, vacancy-agglomerates and dislocations. To achieve a sufficient accuracy within the interesting temperature intervals but to simultaneously limit the annealing time exposure, the temperature steps ΔT were varied between 10 K and 30 K. The corresponding holding times τ were adapted so that $\Delta T/\tau = 10\text{K}/10\text{min}$. With some quantities measured in this thesis, this heating rate could not be realized but in view of the comparably large error bars, the influence on the measured quantity can be considered to be negligible.

Chapter 6

Results

In what follows, an overview of the results is given separately for each chosen metal-defactant system. In the Pd-H system all errors were determined as a standard deviation, $\sigma = \sqrt{\sigma^2}$ as usual. However, in the Fe-C system, the standard error of the mean, $\sigma_M = N^{-1/2} \sigma$ with N as the total number of individual measurement points was used for XLPA and microhardness measurements, and the curves were averaged for Fe-C and pure Fe, respectively. These actions appeared necessary to obtain a significant statistics for the Fe-C system. They were possible not at least because the parameters of consolidation and deformation had no significant influence, neither on the XLPA nor on the microhardness measurements of Fe-C and pure Fe, respectively (see Fig. 6.17).

6.1 Defects in the Pd-H system

To analyze the impact of the different deformation-induced lattice defects on the macroscopic strength it is suitable to investigate the HPT-processed samples and the CR-deformed separately since they show very different von-Mises equivalent strains which affect the macroscopic strength in very different ways.

6.1.1 HPT-processed samples

Calorimetry

Figs. 6.1 and 6.2 depict some of the obtained calorimetry plots [58]. Fig. 6.1 shows the DSC plot of Pd hydrogenated up to $H/Pd = 0.0025$ and deformed at RT to $\epsilon_{vM} = 116$ (black line), as well as deformed at $T = 194$ K (blue line), under the same conditions. Additionally, fig. 6.2 visualizes the DSC

plots of four samples, all deformed at room temperature up to $\epsilon_{vM} = 116$ with four different H concentrations, i.e. H/Pd = 0.45 (red), H/Pd = 0.20 (black), H/Pd = 0.0075 (green) and H/Pd = 0.0025 (blue), respectively.

A qualitative analysis in fig. 6.1 shows an overlapping double-peak at

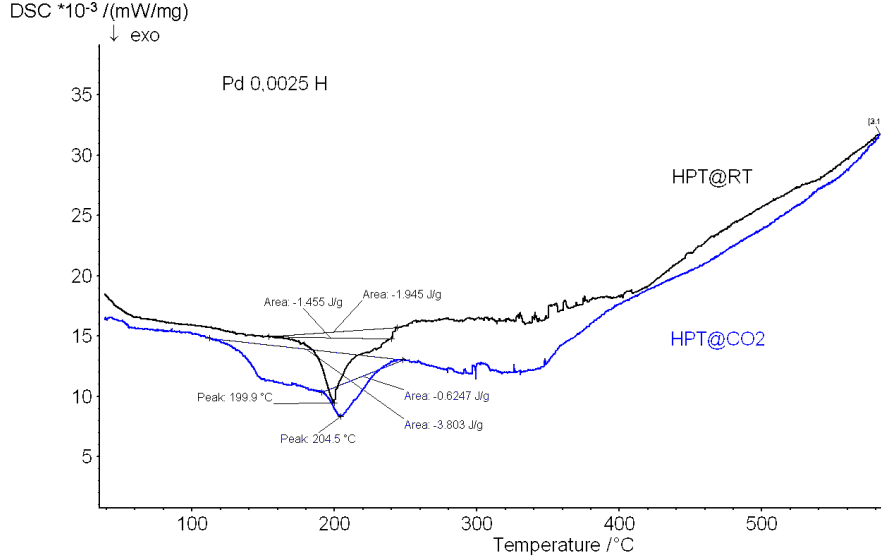


Figure 6.1: DSC plot of Pd-H with H/Pd = 0.0025, deformed at RT (black) and 194 K (blue) [58] .

$T = 200^{\circ}\text{C}$ for $T_{\text{deform}} = \text{RT}$ as well as an overlapping double-peak at $T = 204^{\circ}\text{C}$ for $T_{\text{deform}} = 194\text{ K}$. Both double-peaks indicate the annealing of mono-vacancies and vacancy-agglomerates [12][57]. Furthermore, in fig. 6.2 one can see the same trend for all four samples indicating a similar behavior of all four samples. All four plots show exothermic peaks in a temperature range between 145°C ($0.23T_m$) and 200°C ($0.26T_m$) indicating the annealing of vacancy-type lattice defects [12][57][59]. Since often overlapping double-peaks were found in this temperature range a discrimination of the annealing of single vacancies and vacancy-agglomerates is too difficult if it is based solely on DSC plots. Therefore, a discrimination had to be based on several complementary measurement techniques (see below). In addition to the vacancy peaks also dislocation peaks were found for two samples with H concentrations of H/Pd = 0.45 and H/Pd = 0.20 at $T = 275^{\circ}\text{C}$ (H/Pd = 0.45) and $T = 285^{\circ}\text{C}$ (H/Pd = 0.20), respectively.

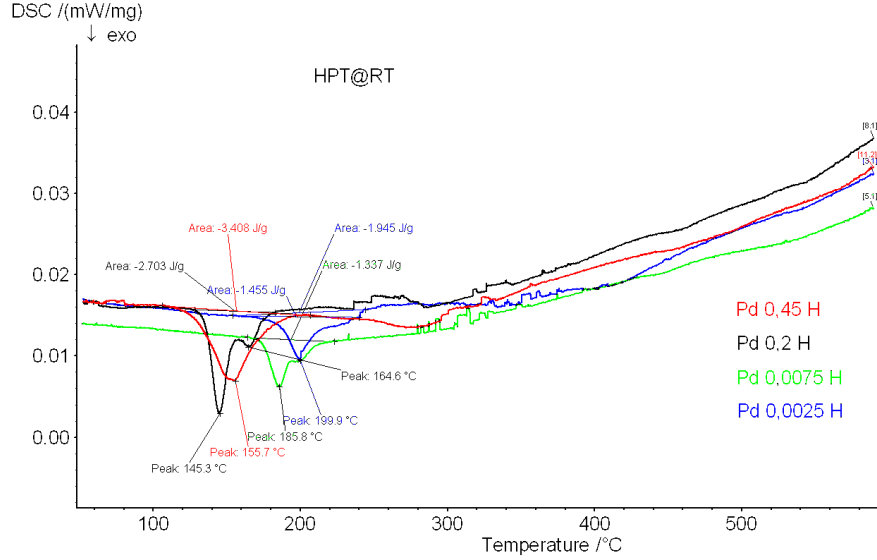


Figure 6.2: DSC plot of Pd-H deformed at RT with H/Pd = 0.45 (red), H/Pd = 0.20 (black), H/Pd = 0.0075 (green) and H/Pd = 0.0025 (blue), respectively [58] .

Dislocation Densities & Crystallite Sizes

A typical evolution of the dislocation density during isochronal annealing is given in fig. 6.3 for two samples, each hydrogenated up to H/Pd = 0.0075 and HPT deformed to a von-Mises equivalent strain of $\epsilon_{vM} = 116$. One sample was deformed at 194 K (blue diamonds) while the second one was deformed at room temperature (brown squares). A non-hydrogenated sample (dark green dashed line) deformed under the same condition is also given and may serve as reference with respect to the impact of hydrogenation. The dislocation density detected at room temperature is $3.2 \times 10^{15} m^{-2}$ ($T_{deform} = RT$) and $3.5 \times 10^{15} m^{-2}$ ($T_{deform} = 194 K$), respectively. These values are constant during isochronal annealing up to a homologous temperature of $T = 0.32T_m$ and decrease rapidly above that temperature. Furthermore, the dislocation density of the non-hydrogenated sample is decreasing steadily from the beginning. Therefore, retrospective, the dislocations in the hydrogenated samples can be considered as stabilized by solute hydrogen.

Moreover, it can be found that the deformation temperature has no significant impact on the dislocation density as the curves for both T_{deform} are the same within the measuring accuracy. Fig. 6.4 provides a survey of the development of the dislocation densities during isochronal annealing of four

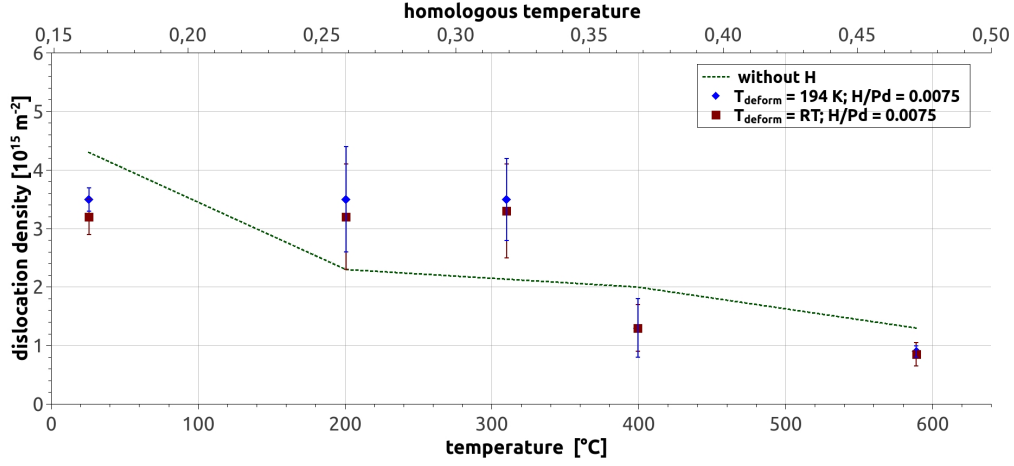


Figure 6.3: Isochrones of dislocation density of HPT-deformed, Pd-H with $\text{H/Pd} = 0.0075$, deformed at 194 K (blue diamonds) and room temperature (brown squares). Deformed without hydrogen as reference (dark green dashed line)

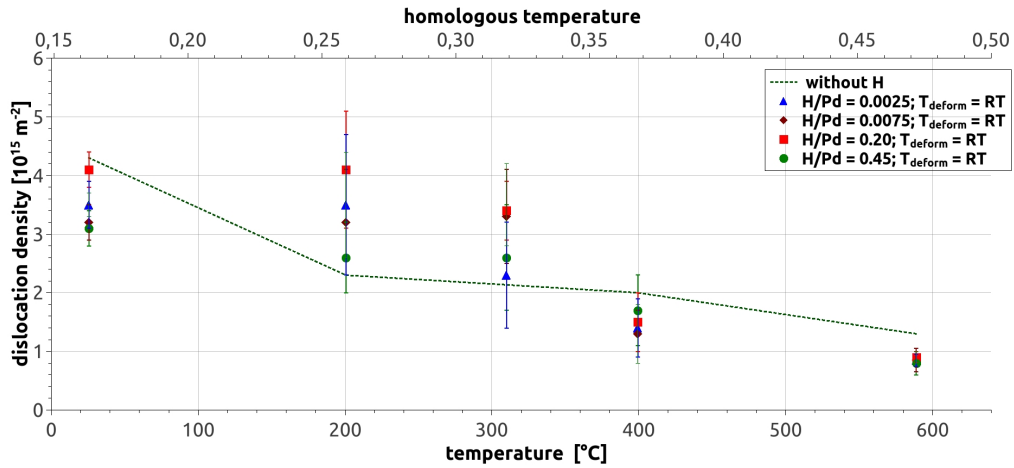


Figure 6.4: Isochrones of dislocation density with different H/Pd ratios, deformed at RT. $\text{H/Pd} = 0.45$ (green circles), $\text{H/Pd} = 0.20$ (red squares), $\text{H/Pd} = 0.0075$ (brown diamonds) and $\text{H/Pd} = 0.0025$ (blue pyramids). Deformed without hydrogen as reference (dark green dashed line)

samples with four different hydrogen concentrations, i.e. $\text{H/Pd} = 0.45$ (green

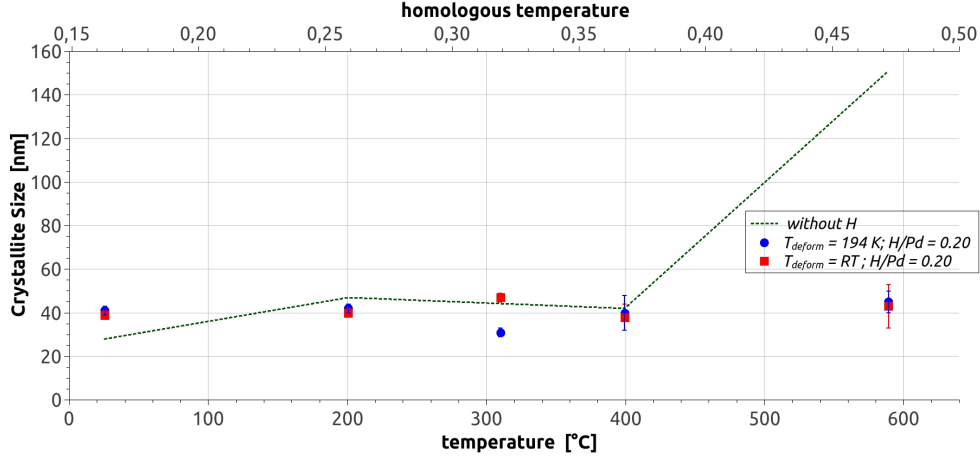


Figure 6.5: Isochrones of crystallite size of HPT-deformed, Pd-H with $H/Pd = 0.20$, deformed at 194 K (blue circles) and room temperature (red squares). Deformed without hydrogen as reference (green dashed line)

circles), $H/Pd = 0.20$ (red squares), $H/Pd = 0.0075$ (brown diamonds) and $H/Pd = 0.0025$ (blue pyramids), and HPT deformed at room temperature up to a von-Mises equivalent strain of $\epsilon_{vM} = 116$. A non-hydrogenated sample deformed under the same conditions is also given (dark green dashed line). All hydrogenated samples show the same trend discussed in detail for fig. 6.3. The variations between the different hydrogen concentrations is within maximum approx. $\pm 10\%$ and is negligible for the highest measured homologous temperature. No correlation between the initial hydrogen concentration and the dislocation density can be determined.

In order to investigate the influence of subgrain boundaries on the macroscopic strength in hydrogenated and severely deformed Pd the evolution of the crystallite size, D , during isochronal annealing was analyzed via XLPA. The obtained isochrone by crystallite size for samples with $H/Pd = 0.20$ and $\epsilon_{vM} = 116$ is shown in fig. 6.5 where blue circles depict the sample deformed at 194 K while red squares represent the sample processed at room temperature. A non-hydrogenated sample (dark green dashed line) processed under the same conditions is also given.

The crystallite sizes of all Pd-H samples are constant at (40 ± 7) nm over the whole temperature range measured. Therefore, it has to be concluded that the grain size does not vary significantly over the whole temperature range. Beside one can see from fig. 6.5 that the deformation temperature has no influence on the crystallite size since both curves for both T_{deform} are identical.

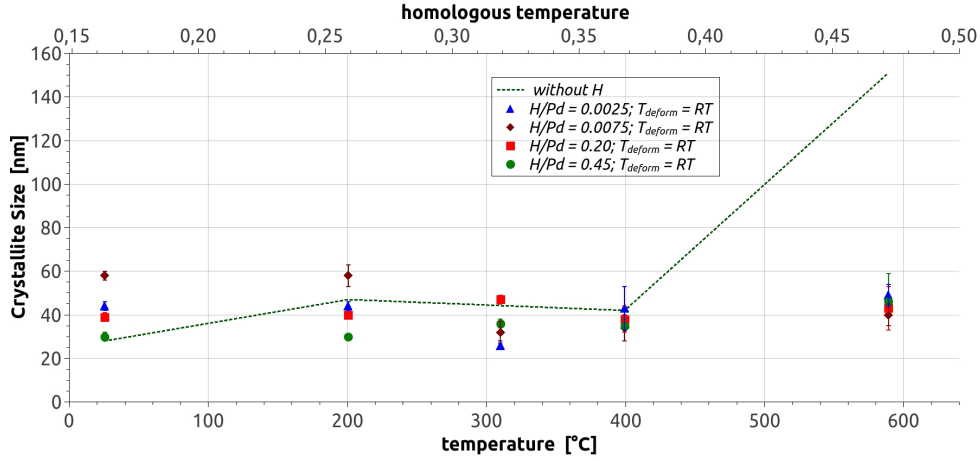


Figure 6.6: Isochrones of crystallite size with different H/Pd ratios, deformed at RT. H/Pd = 0.45 (green circles), H/Pd = 0.20 (red squares), H/Pd = 0.0075 (brown diamonds) and H/Pd = 0.0025 (blue pyramids). Deformed without hydrogen as reference (green dashed line)

Furthermore, fig. 6.6 visualizes the progress in crystallite size during annealing of samples with all four different hydrogen concentrations and exhibits a roughly constant crystallite size over the whole temperature range. This emphasizes that the constant subgrain size is both independent of the deformation temperature as well as nearly independent of the initial hydrogen concentration. Moreover, the development of the non-hydrogenated sample differs a lot, especially at $T > 0.37T_m$, from the hydrogenated ones, see figs. 6.5 and 6.6, and hence a stabilization of the crystallite size by solute H must be presumed.

Microhardness

A typical isochrone by microhardness obtained via successive annealing of a hydrogenated and deformed Pd sample with H/Pd = 0.45 and $T_{deform} = RT$ (blue squares) as well as a non-hydrogenated one (dark green dashed line), serving as reference, is shown in fig. 6.7. One can see an enormous increase in microhardness from about 0.5 GPa (cf. table 1.1) to 1.83 GPa (which is a gain of microhardness by a factor 3.6) if well annealed Pd is severely plastically deformed up to $\epsilon_{vM} = 116$ without hydrogenation. An additional increase of about 0.79 GPa (43%) can be found when hydrogenating the

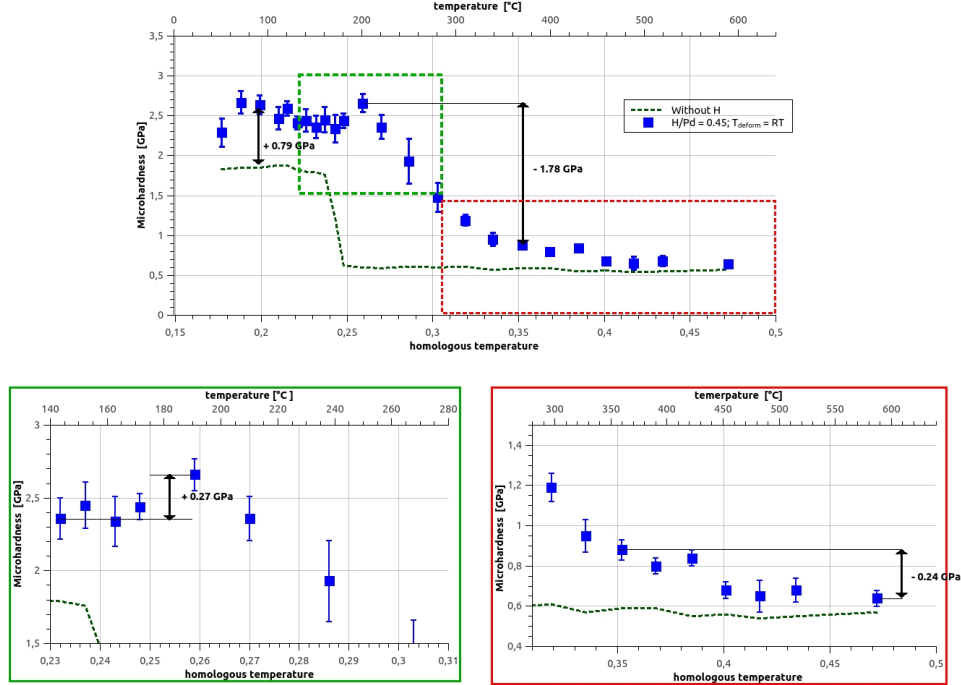


Figure 6.7: Isochrone by microhardness for a sample deformed at RT with $H/Pd = 0.45$ (blue squares) and deformed without H as reference (dark green dashed line)

Pd up to $H/Pd = 0.45$ before deformation. This result gives a hint on the stabilization of deformation-induced lattice defects and thus a gain in microhardness due to solute H in pure Pd. It also indicates the same trend that Chen et al. investigated in cold rolled Pd in 2013 [13] and 2015 [37] as discussed above.

In the temperature range between $0.24T_m$ and $0.27T_m$ (framed green and zoomed in) a peak in microhardness of about 0.27 GPa (11%) was found. This peak is of crucial importance, as will be discussed in the next chapter. This obtained isochrone exhibits another distinctive feature in the temperature range from $0.27T_m$ to about $0.35T_m$. In this range a tremendous decrease in microhardness of about 1.78 GPa (67%) was found. In addition, a comparison of the hydrogenated sample with the reference and in respect of this enormous decrease in microhardness demonstrates some more detail. The temperature of the huge decrease, occurring qualitatively in both the hydrogenated and the non-hydrogenated sample, is lower (approx. 90 K) for the

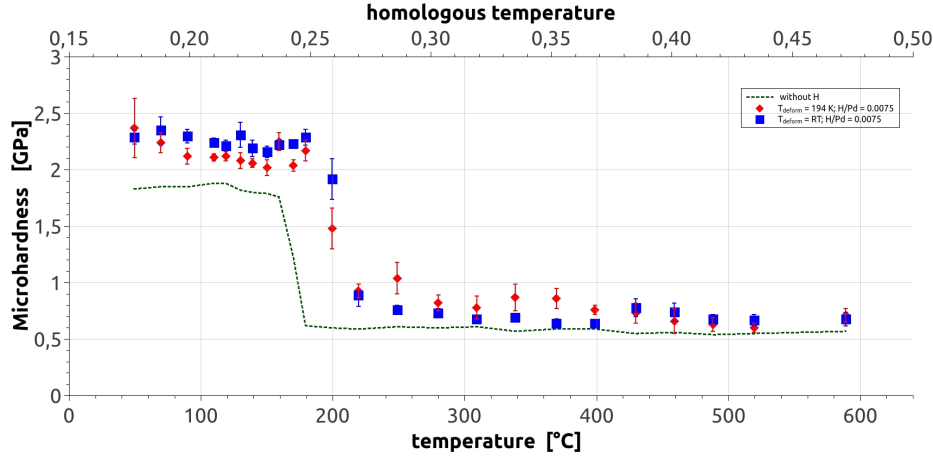


Figure 6.8: Isochrone by microhardness with different deformation temperatures and $H/Pd = 0.0075$; deformed at RT (blue squares) and at 194 K (red diamonds); deformed without H at RT as reference (dark green dashed line)

reference than for the hydrogenated sample. Finally a decrease of about 0.24 GPa (9%) can be found in the isochrone for $T > 0.35T_m$ (framed red and zoomed in).

In order to investigate the influence of the processing temperature during SPD deformation samples with two different deformation temperatures were measured. Fig. 6.8 shows the obtained results. One sample was deformed at RT (blue squares) and a second one at 194 K (red diamonds). Both samples were deformed up to $\epsilon_{vM} = 116$ with a H concentration of $H/Pd = 0.0075$. As reference a non-hydrogenated sample deformed at room temperature is given (dark green dashed line).

The impact of the H concentration on the macroscopic strength can be studied from fig. 6.9. Here the isochronal microhardness of HPT-processed Pd (up to $\epsilon_{vM} = 116$ and $T_{deform} = RT$) with four different H concentrations, i.e. $H/Pd = 0.45$ (blue squares), $H/Pd = 0.20$ (red diamonds), $H/Pd = 0.0075$ (brown triangles) and $H/Pd = 0.0025$ (light green pyramids) is depicted. A reference (dark green dashed line) of a non-hydrogenated Pd deformed under the same conditions is also given. For all four H concentrations the maximum microhardness can be observed at a temperature of $T(HV_{max}) = (190 \pm 10)^\circ C$.

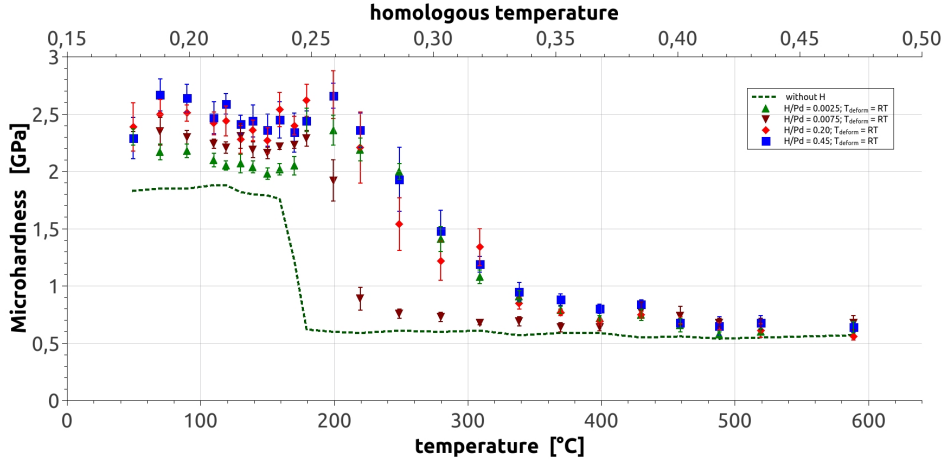


Figure 6.9: Isochrone by microhardness with different H/Pd ratios, deformed at RT. H/Pd = 0.45 (blue squares), H/Pd = 0.20 (red diamonds), H/Pd = 0.0075 (brown triangles) and H/Pd = 0.0025 (light green pyramids). Deformed without H as reference (dark green dashed line)

6.1.2 CR processed samples

While HPT processing of Pd-H yielded in a von-Mises equivalent strain of $\epsilon_{vM} = 116$ that of CR processed Pd-H resulted in a much smaller equivalent strain of $\epsilon_{vM} \approx 0.75$. Therefore, the obtained results presented in the following sections are less distinct. Furthermore, the investigations on HPT-processed Pd-H exhibited no dependence on the deformation temperature and thus the CR deformed samples were investigated with cold rolling only at room temperature.

Calorimetry

The findings of the DSC investigations on hydrogenated (green line) and non-hydrogenated (blue line) Pd deformed up to a von-Mises equivalent strain of $\epsilon_{vM} \approx 0.73$ are visualized in fig. 6.10 where the hydrogenated sample had an initial H concentration of H/Pd = 0.0075. The DSC plot of the non-hydrogenated sample shows a small exothermic peak at $T = 124^\circ\text{C}$ presenting an annealing of single vacancies [12][57][59]. A pronounced exothermic peak can be found at $T = 283^\circ\text{C}$ determining an annealing of vacancy-agglomerates [12][57]. Additionally, an exothermic peak at $T = 488^\circ\text{C}$ can be seen. This peak is characteristic for an annealing of dislocations [12][57][59].

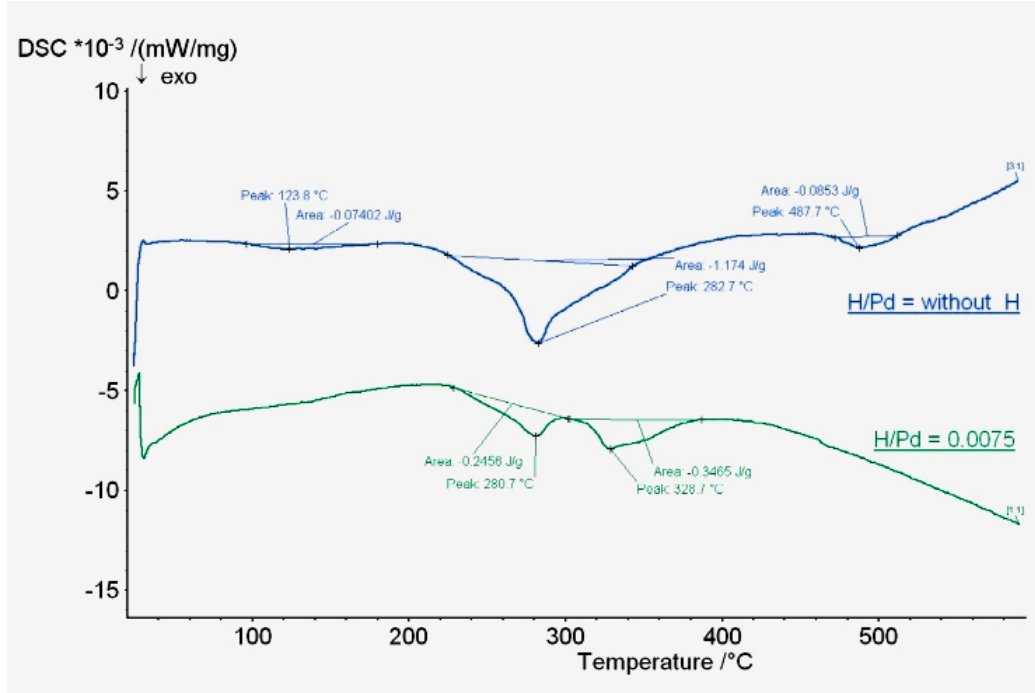


Figure 6.10: DSC plot of Pd-H, deformed via CR up to $\epsilon_{vM} \approx 0.75$ with $H/Pd = 0.0075$ (green line) and without H (blue line)

Moreover, in the calorimetry plot of the Pd-H sample the exothermic peak of single vacancies has disappeared and also the dislocation peak is no more detectable. Furthermore, it can be seen from fig. 6.10 that the characteristic peak of vacancy-agglomerates is split into two separate peaks.

Dislocation Densities & Crystallite Sizes

In fig. 6.11 the development of the dislocation density, ρ , during successive isochronal annealing of a Pd-H with $H/Pd = 0.0075$ (red squares) and subsequently cold rolled up to $\epsilon_{vM} = 0.73$, is visualized. The dislocation density of a non-hydrogenated sample (blue diamonds) and deformed under the same conditions is also given and may serve as reference. The isochrones of the hydrogenated and the non-hydrogenated sample appear to be similar, indicating no significant influence of the solute hydrogen. However, both isochrones showed a slight decrease in dislocation density with $\Delta\rho \approx 1.6 \times 10^{15} m^{-2}$ in the temperature range from $T = 0.16T_m$ to $T = 0.32T_m$. Moreover, a very small increase in dislocation density ($\Delta\rho \approx 0.5 \times 10^{15} m^{-2}$) can be observed in the temperature interval from $T = 0.32T_m$ to $T = 0.37T_m$. At last, a small decrease in dislocation density of $\Delta\rho \approx 1.3 \times 10^{15} m^{-2}$ occurs at $T > 0.37T_m$.

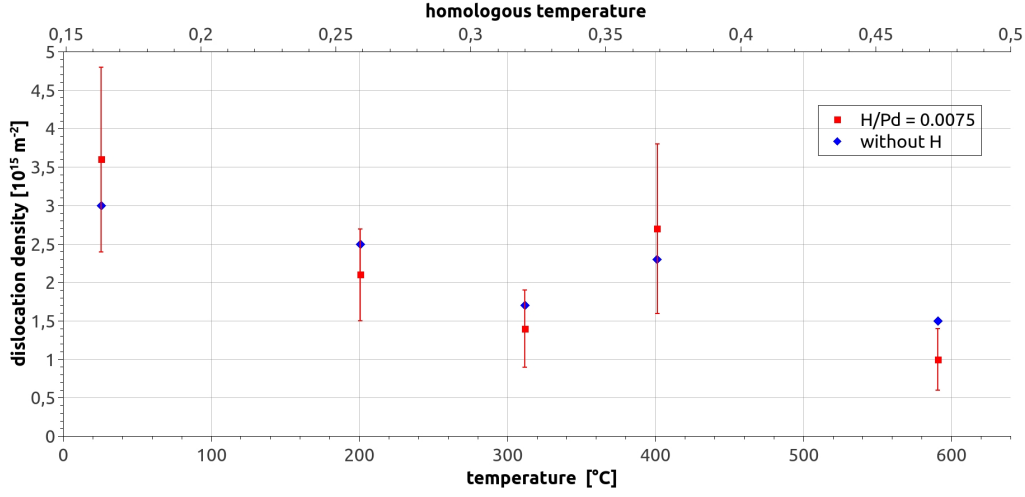


Figure 6.11: Isochrone by dislocation density of CR-deformed Pd-H with $\text{H/Pd} = 0.0075$ (red squares) and deformed without hydrogen as reference (blue diamonds)

Investigations on the influence of subgrain boundaries in cold rolled Pd-

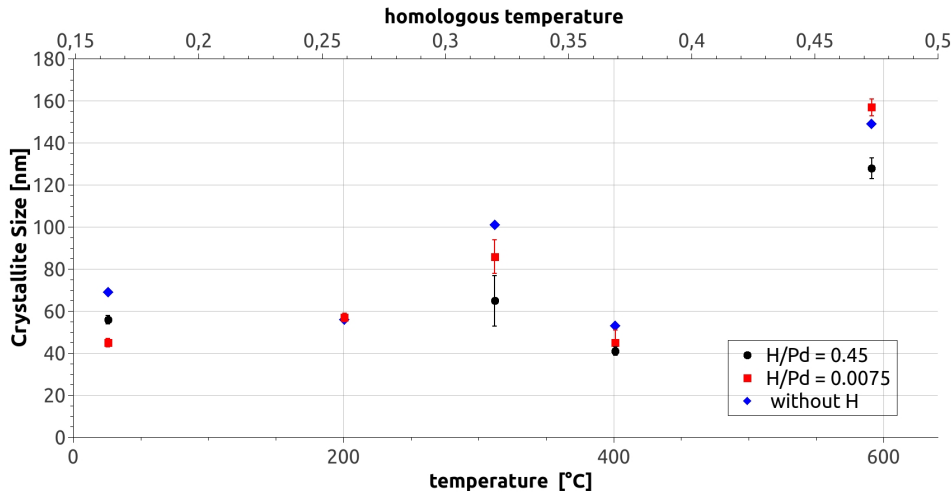


Figure 6.12: Isochrone by crystallite size of CR-deformed, Pd-H. $\text{H/Pd} = 0.45$ (black circles), $\text{H/Pd} = 0.0075$ (red squares) and deformed without hydrogen as reference (blue diamonds)

H were performed by measurements of the crystallite size, D , which are shown in fig. 6.12 where blue diamonds denote the crystallite sizes of a non-hydrogenated sample, red squares represent the values of samples with

H/Pd = 0.0075, and black circles depict crystallite sizes of samples with an initial hydrogen concentration of H/Pd = 0.45, respectively. All samples were processed at room temperature by CR up to a von-Mises equivalent strain of $\epsilon_{vM} \approx 0.75$. Since an influence of the concentration of solute hydrogen was not determined, all three isochrones appear to be similar.

Below a homologous temperature of $T \lesssim 0.26T_m$ the crystallite size was approximately constant at $D \approx 60 \text{ nm}$. In addition, a slight increase in crystallite size of $\Delta D \approx 35 \text{ nm}$ was observed at a homologous temperature of $T = 0.32T_m$. Furthermore, the isochrone shows a decrease in crystallite size of the same ΔD value around a homologous temperature of $T \approx 0.37T_m$. At last, at a homologous temperature above $T > 0.37T_m$ a significant increase in crystallite size of $\Delta D = 99 \text{ nm}$ could be observed.

Microhardness

The evolution of the microhardness during successive isochronal heating of a non-hydrogenated (blue dashed line) as well as a hydrogenated (red squares) Pd sample with an initial H concentration of H/Pd = 0.0075 and cold rolled to about 50% of the initial thickness is shown in fig. 6.13. Like the HPT-processed samples before the hardness of a well annealed Pd, cold rolled up to a von-Mises equivalent strain of $\epsilon_{vM} \approx 0.73$, is risen, here from about 0.5

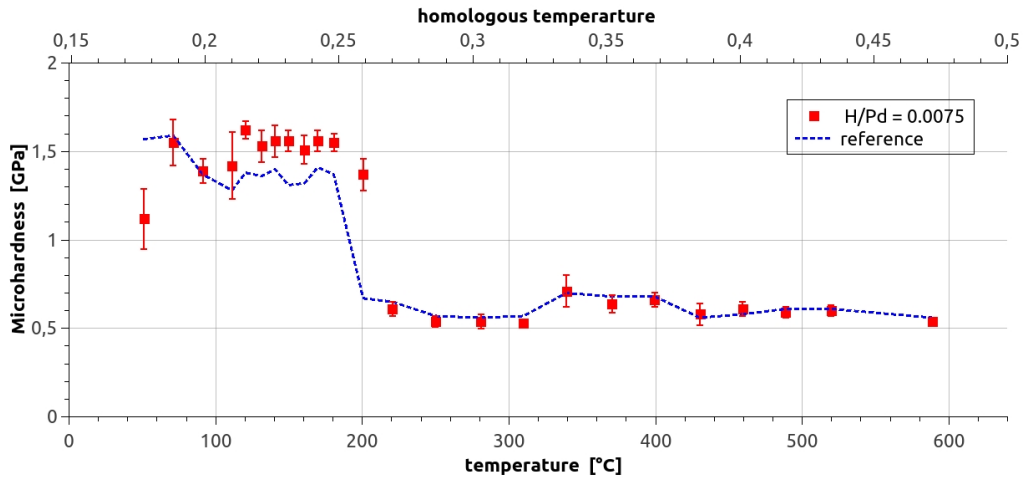


Figure 6.13: Isochrone by microhardness for a sample deformed via CR at RT with H/Pd = 0.0075 (red squares) and deformed without H as reference (blue dashed line)

GPa (cf. table 1.1) to 1.59 GPa, i.e. an increase in microhardness by a factor 3.0.

Nevertheless, in the temperature range between $0.24T_m$ and $0.27T_m$ a large decrease in microhardness ($\Delta HV = 1.0 \text{ GPa}$) was found. Moreover, in fig. 6.13 a slight increase in microhardness ($\Delta HV = 0.1 \text{ GPa}$) can be seen around $T = 0.30T_m$. At last, the isochrone by microhardness exhibits a slight decrease ($\Delta HV = 0.11 \text{ GPa}$) at a homologous temperature of $T = 0.37T_m$.

6.2 Defects in the Fe-C system

In order to check the hypothesis that C can act as defactant in Fe and therefore might have a significant impact on the macroscopic strength by stabilization of different deformation-induced lattice defects, measurements during successive isochronal annealing of Fe0.8wt%C and of pure Fe were performed. The obtained results are shown in the following sections.

6.2.1 HPT-processed samples

Calorimetry

In order to investigate the type and concentration of deformation-induced lattice defects in consolidated and deformed Fe0.8wt%C powder as well as in pure Fe after HPT-processing DSC plots were obtained. Fig. 6.14 (a) visualizes the results of ball milled Fe0.8wt%C powders consolidated at two different pressures, i.e. 4 GPa (blue and brown lines) and 6 GPa (red line), and deformed up to three different von-Mises equivalent strains, i.e. $\epsilon_{vM} = 83$ (red line), $\epsilon_{vM} = 207$ (blue line) and $\epsilon_{vM} = 417$ (brown line), respectively. Additionally, fig. 6.14 (b) gives the achieved DSC curves of pure Fe powder consolidated at a pressure of 6 GPa and deformed up to $\epsilon_{vM} = 83$ (green line) and $\epsilon_{vM} = 207$ (dark blue line), respectively.

A qualitative analysis shows a good agreement of the three curves of the Fe-C samples, fig. 6.14 (a), with respect to the temperatures of the exothermic peaks. The same agreement can be found for the two DSC plots of the pure Fe samples, fig. 6.14 (b).

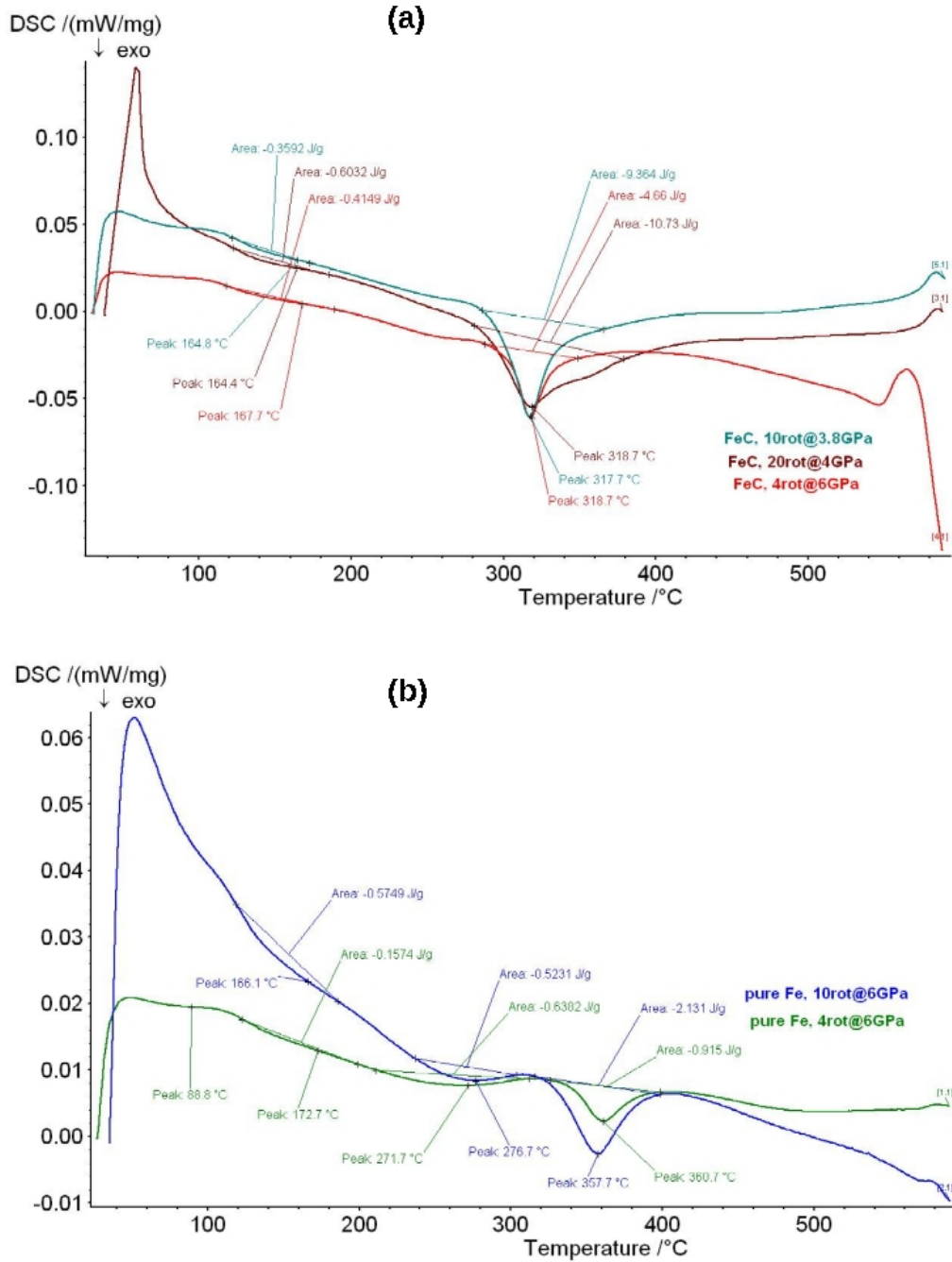


Figure 6.14: DSC plots of solid samples of (a) Fe0.8wt%C and (b) pure Fe with different von-Mises equivalent strains

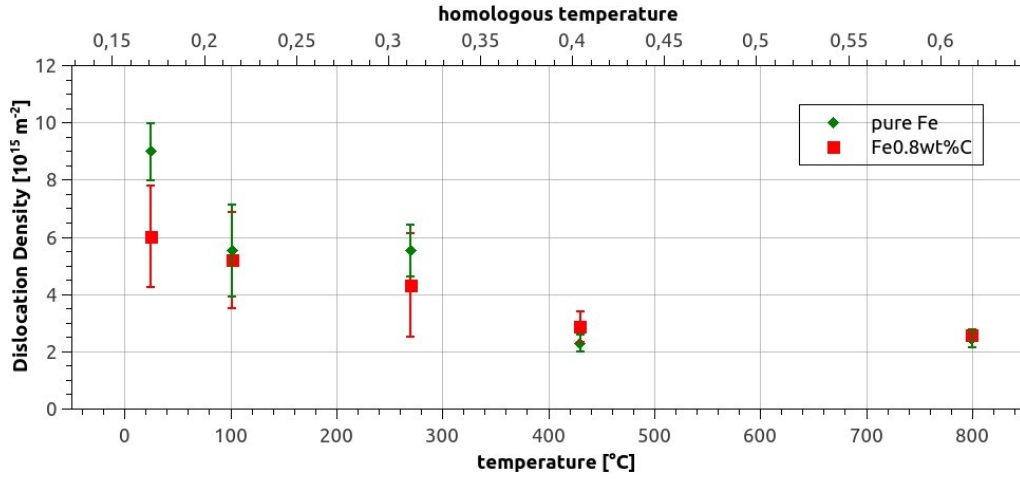


Figure 6.15: Isochrone by dislocation density of pure Fe (green diamonds) and Fe0.8wt%C (red squares)

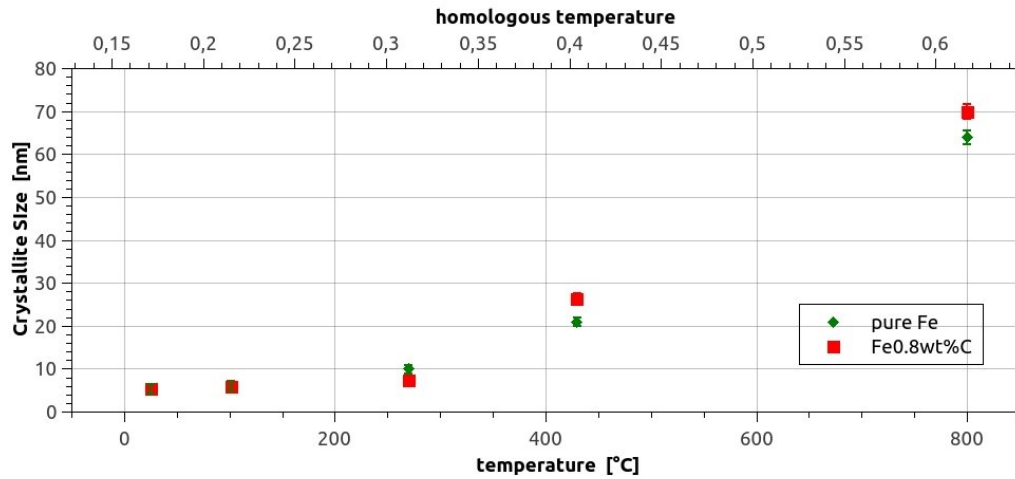


Figure 6.16: Isochrone by crystallite size of Fe0.8wt%C (red squares) and pure Fe (green diamonds)

Dislocation Densities & Crystallite Sizes

In order to separate the influence of vacancies on the macroscopic strength from that of dislocations XLPa was performed and the isochrone by dislocation density shown in fig. 6.15 was obtained. Red squares depict the dislocation densities of Fe-C samples while green diamonds represent those of pure Fe samples.

As can be seen, the dislocation density of the Fe-C sample is decreasing by

$\Delta\rho \approx 3.4 \times 10^{15} m^{-2}$ over the whole interval of annealing temperatures or by $\Delta\rho \approx 1.5 \times 10^{15} m^{-2}$ for $T > 0.35T_m$.

A similar impression can be received for pure Fe. Also the dislocation density of pure Fe is decreasing by $\Delta\rho \approx 6.5 \times 10^{15} m^{-2}$ over the whole temperature range or by $\Delta\rho \approx 3.1 \times 10^{15} m^{-2}$ for $T > 0.35T_m$.

To get an idea of the impact of the subgrain size on the macroscopic strength of Fe-C as well as of pure Fe XLPAs was performed with respect to the crystallite size, D . Fig. 6.16 is visualizing the obtained isochrone. It was found that the crystallite size is constant at $D \approx 7 \text{ nm}$ below a homologous temperature of $0.35T_m$ and is increasing tremendously above this temperature up to $D \approx 67 \text{ nm}$ for both, the pure Fe and the Fe-C samples.

Microhardness

The development of the microhardness during isochronal annealing of consolidated and deformed Fe0.8wt%C under three different parameters is shown in fig. 6.17 (a) while that of pure Fe with two different parameters of consolidation and deformation is given in fig. 6.17 (b). One can see that the individual curves are quite similar for both graphs. Thus neither the pressure of consolidation nor the number of rotations during HPT-processing have a significant influence on the results of the microhardness. Thus both the XLPAs as well as the microhardness measurements presented in Fig. 6.18, of Fe-C (red squares) and pure Fe (green diamonds) can be averaged, and added by the mean error of the mean. Below a homologous temperature of $0.30T_m$ both curves of Fe-C and pure Fe appear to be similar. However, Severe Plastic Deformation on ball milled powders increased the microhardness of Fe-C and pure Fe up to $HV \approx 10 \text{ GPa}$ which is a gain in hardness by a factor of about 2 compared to commercial bulk samples of Fe0.8wt%C (cf. Table 1.2) and by a factor of ~ 6 in comparison to pure Fe bulk samples, respectively. In the temperature range from $0.30T_m$ to $0.35T_m$ the microhardness of Fe-C shows a peak of $\Delta HV \approx 1 \text{ GPa}$ (9%) while the hardness of pure Fe remains approximately constant. For $T > 0.35T_m$ the microhardness is continuously decreasing by $\Delta HV \approx 6 \text{ GPa}$ ($\sim 50\%$), for both the Fe-C and the pure Fe.

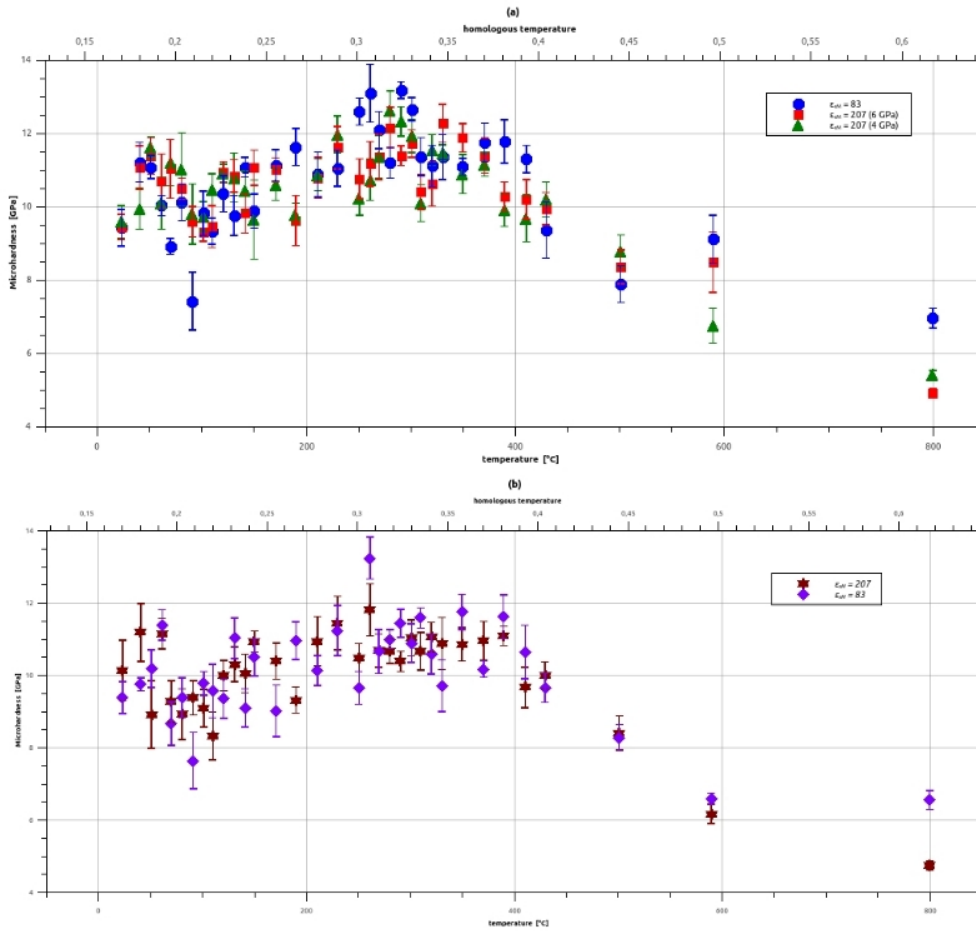


Figure 6.17: Isochrones by microhardness of (a) Fe-C samples with varying consolidation parameters and (b) of pure Fe samples with different consolidation parameters

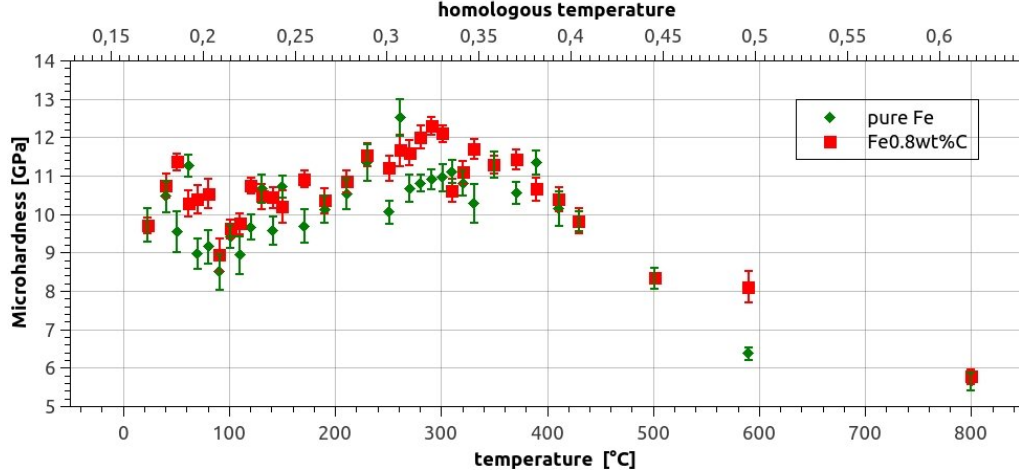


Figure 6.18: Isochrone by microhardness of Fe0.8wt%C (red squares) and pure Fe (green diamonds)

6.2.2 BM-processed samples

Consolidation and deformation of ball milled Fe0.8wt%C powder by HPT yielded in a von-Mises equivalent strains of $\epsilon_{vM} = 83$, $\epsilon_{vM} = 207$ and $\epsilon_{vM} = 414$, respectively. In order to compare the results with that of much higher ϵ_{vM} and to analyze the evolution of deformation-induced lattice defects during consolidation and deformation via HPT, the same measurements were carried out on the as-milled powders.

Calorimetry

For a DSC measurement 120 mg of the Fe-C powder was filled loosely under protective atmosphere in a DSC pan (material: Al) and shut with an appropriate cap via a hand press. Fig. 6.19 shows the obtained DSC plot for the ball milled Fe0.8wt%C powder (green line). For comparison a sample consolidated and deformed with a pressure of 4 GPa up to a von-Mises equivalent strain of $\epsilon_{vM} = 414$ is also given (brown line). In both curves an exothermic peak around $T \approx 140^\circ\text{C}$ can be found representing the annealing of single vacancies. Additionally, a second exothermic peak is visible in both graphs around $T = 319^\circ\text{C}$ indicating the annealing of vacancy agglomerates superposed with an annealing of dislocations.

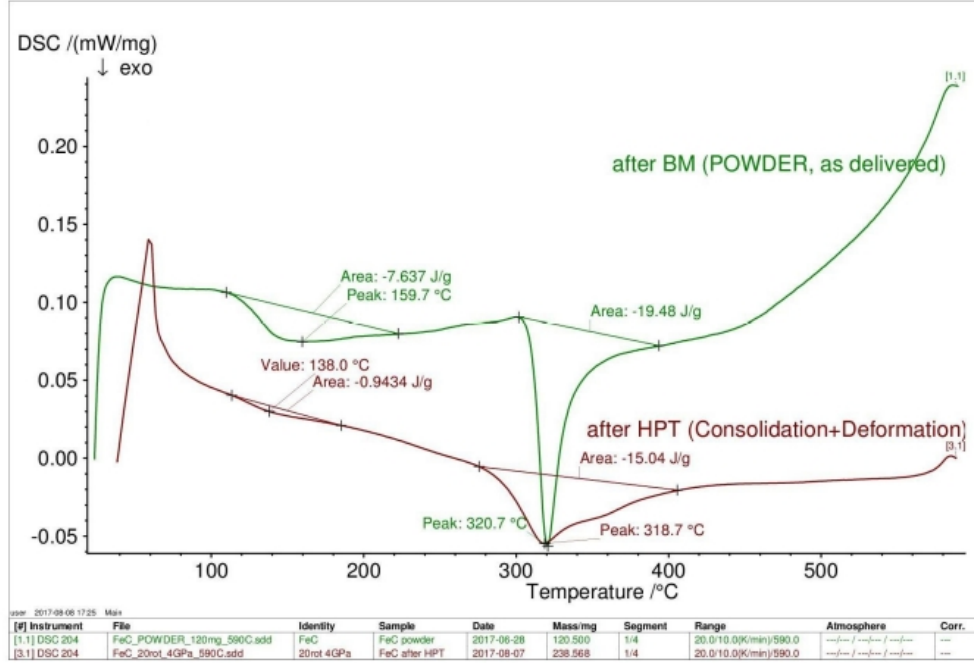


Figure 6.19: DSC plot of Fe0.8wt%C powder after ball milling (green line) and after milling, consolidation and deformation (brown line)

Dislocation Densities & Crystallite Sizes

For XLPA Fe0.8wt%C powder was guarded compacted with 0.4 GPa via a hand press and a X-ray line profile was measured at room temperature as well as after annealing at an elevated temperature. Fig. 6.20 compares the obtained isochrone by dislocation density (full symbols) and crystallite size (empty symbols) of a consolidated (at 4 GPa) and deformed (up to $\epsilon_{vM} = 20$) Fe-C powder (red) with the dislocation densities determined for the as-milled powder (blue) at room temperature and annealed at an elevated temperature. As can be seen, both the dislocation density and the crystallite size of the powder are of the same order of magnitude as well as the same trends as those of additionally consolidated and deformed Fe-C. It is therefore clear that consolidation and deformation of balled milled powder has no significant impact neither on the dislocation density nor on the crystallite size.

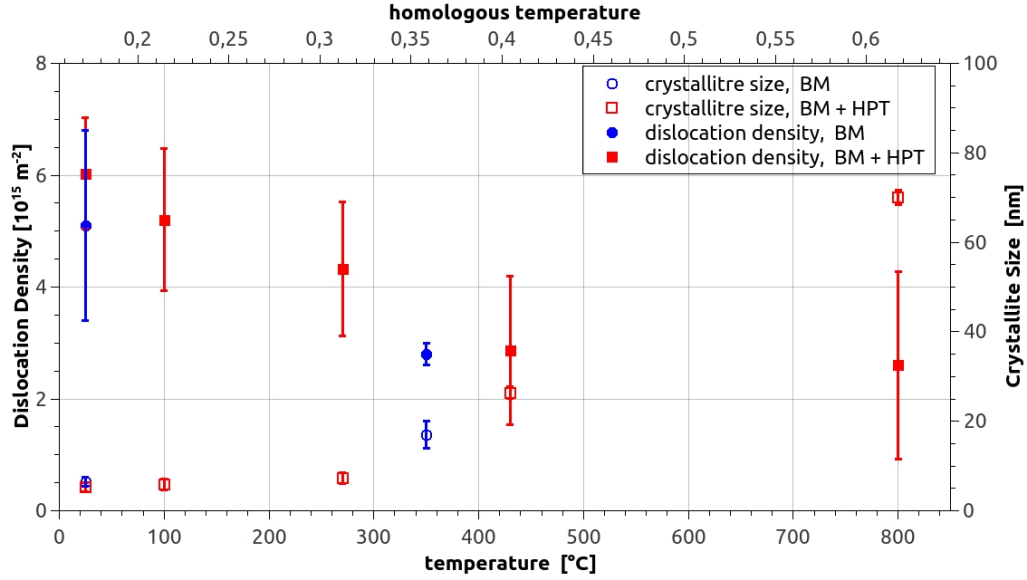


Figure 6.20: Dislocation density (full symbols) and crystallite size (empty symbols) of Fe0.8wt%C after ball milling (blue) and after milling, consolidation and deformation (red)

Microhardness

Additional values of the microhardness of the ball milled powder could not be measured for technical reasons.

Chapter 7

Discussion

In the following sections it is possible to answer the research questions arisen in chapter 3 "Aims of research", on the basis of results presented in chapter 6. Each metal-defactant system is discussed separately. At first in section 7.1.1. for one selected example, a presentation of all the different isochrones is done simultaneously, in order to identify the thermal events behind the steps. Such a comparison ends up with quite small figures; details of them may be taken from the analogous figures given in ch. 6 "Results" or in the sections following to 7.1.1 .

7.1 Pd-H

7.1.1 HPT-processed state

Common qualitative discussion of results

Fig. 7.1 visualizes the isochrones gained from Pd-H with a H concentration of $H/Pd = 0.45$ deformed via HPT up to a von-Mises equivalent strain of $\epsilon_{vM} = 116$ at two different temperatures, i.e. room temperature and $-79^\circ C$, respectively. In figs. 7.1 (b), (c) and (d) the values of a sample deformed without H are given as reference (green dashed line).

Most importantly, in the DSC plot shown in fig. 7.1 (a) [58], one can see a significant exothermic peak around $T = 150^\circ C$ for both samples that deformed at RT (black line) and that deformed at $-79^\circ C$, named *CO2*. According to our group's works and the literature [12] [57], this peak is due to the annealing of vacancy agglomerates. Further exothermic peaks at higher temperatures appear between $T = 300^\circ C$ and $T = 350^\circ C$, which may be due to the annealing of HPT induced dislocations.

For further confirmation of the peaks' interpretation, we can inspect the an-

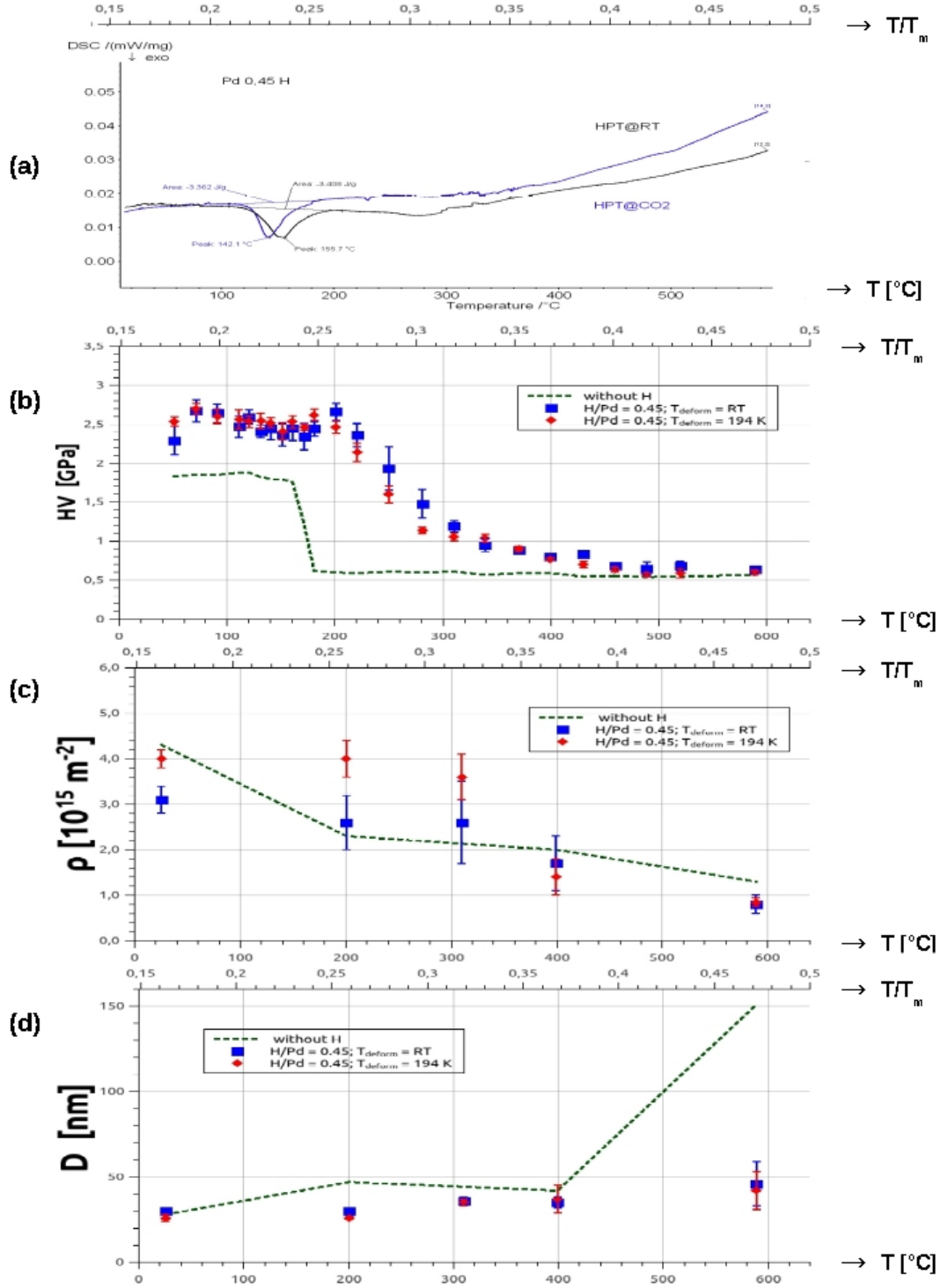


Figure 7.1: Comparison of correlated isochrones, i.e. (a) DSC plot [58], (b) microhardness HV, (c) dislocation density ρ (XLP) and (d) crystallite size D (XLP), of Pd-H with H/Pd = 0.45 **processed via HPT** at different T; (a): deformed at RT (—) and at 194K (■); (b), (c) and (d): deformed without H at RT (—), hydrogenated and deformed at RT (■) and at 194K (◆)

nealing characteristics of the **dislocation density** measured by XLPD and shown in fig. 7.1 (c). In the temperature range till about $T = 300^\circ\text{C}$, it is constant which substantiates the conclusion that the low-temperature DSC peak is due vacancy agglomerations, while that of higher temperatures can be attributed to the annealing of dislocations. Obviously, most of those dislocations are part of subgrain boundaries at least those annealing beyond $T = 400^\circ\text{C}$, as the crystallite size, fig. 7.1 (d), starts to increase after being constant at lower annealing temperatures.

We can now use the characteristics of **microhardness isochrones**, fig. 7.1 (b), for further substantiation of above conclusions. Close to the temperature range of the low-temperature DSC peak, the isochrone by microhardness, shows an unexpected increase at $T = 0.25T_m = 200^\circ\text{C}$. Since this DSC peak can be identified with the mobilization and annihilation/annealing of vacancies, it must be concluded that agglomeration of vacancies / vacancy agglomerates happens because single vacancies do not hinder the dislocation movement [68]. The hardening effect arises from formation and coarsening of vacancy agglomerates as described in literature [44] [83] [84]. Let us call this annealing stage "stage III" in what follows. In the next higher temperature range $> 200^\circ\text{C}$, an enormous decrease in microhardness occurred, for both HPT-deformation temperatures, RT (blue squares) and CO2 (red diamonds), respectively. Again, this decrease can be only ascribed to an annealing of vacancy agglomerates because within the same temperature range, the dislocation density remains constant, and so does the subgrain size. Let us call this annealing stage as "stage IV" in what follows.

Finally, at $T > 300^\circ\text{C}$ another small decrease in microhardness was obtained. The corresponding isochrone by dislocation density, fig. 7.1 (c), indicated a decrease in the same temperature range. In this range, the crystallite size, fig. 7.1 (d), remained constant or slightly increased. Also the DSC-Plot, fig. 7.1 (a), indicated nothing contradictory.

Therefore, this decrease in microhardness should be ascribed to the annealing of dislocations and/or to the increase of crystallite size. In the following, we shall call this stage which corresponds to the so-called "primary recrystallization stage" in literature [45], to be "stage V" in all following discussions.

Vacancy Concentration

Fig. 6.1 (in chapter "Results") visualized the obtained DSC plots of Pd-H ($\text{H/Pd} = 0.0025$, $\epsilon_{vM} = 116$) deformed at RT and at $T = -79^\circ\text{C}$ in order to investigate the impact of the processing temperature. Moreover, fig. 6.2 depicted the impact of the initial H concentration in the obtained DSC plot. The exothermic peaks were identified to be caused by the annealing

of vacancy-type lattice defects. In about 50% of the samples, another peak around annealing temperatures was found which obviously represents the annealing of dislocations, not at least because of the findings by XLPA which revealed a clear decrease of dislocation density at the same annealing temperature within about $350^\circ < T < 400^\circ\text{C}$. Quantitative analyses revealed the stored energies given in table 7.1. of vacancy annealing peaks of the samples HPT-processed at different temperatures starting with different H/Pd contents. Using eq. 5.7 with $\Delta H_\nu^f = 1.85 \pm 0.01$ eV per vacancy [45][59] and the molar mass $M = 106.42 \times 10^{-3} \text{kg mol}^{-1}$ (cf. table 1.1), the vacancy concentrations and the molar mass $M = 106.42 \times 10^{-3} \text{kg mol}^{-1}$ (cf. table 1.1), the vacancy concentrations c_{Vac} given in table 7.1. were calculated; they range from 0.6 to 2.3×10^{-3} . While the HPT-processing temperature does not affect the vacancy concentrations and dislocation densities significantly, the H-concentration present before HPT-processing appears to enhance c_{Vac} considerably.

In table 7.1, also the stored energies of those samples are given which showed a dislocation peak. Using eq. 5.6, a shear modulus of $G = 42.0$ GPa, a Burgers vector $b = 2.744 \times 10^{-10} \text{m}$, the lattice constant of Pd $a = 0.388$ nm and a Poisson ratio of $\nu = 0.39$ giving to be $\kappa = 0.805$, the dislocation densities ρ , given in table 7.1. could be calculated. In view of the low measurement accuracy because of the generally low stored energies of this peak, the resulting absolute values of ρ do not seem to be too reliable; only a tendency for higher dislocation densities for higher H-contents can be suspected. A much better way to find reliable ρ values is the use of the XLPA method which has been described in ch. 5.3.3. Results of those measurements are given in ch. 6.1.1.

H/Pd	T_{deform}	E_{stor}^{Vac} [J/g]	E_{stor}^{Dis} [J/g]	c_{Vac} [10^{-3}]	ρ [10^{15}m^{-2}]	sample identifier
0.0025	RT	1.455	n/a	0.9	n/a	#7
0.0025	194 K	3.803	n/a	2.3	n/a	#10
0.0075	RT	1.337	n/a	0.8	n/a	#5
0.0075	194 K	1.488	0.50	0.9	5	#9
0.20	RT	2.703	0.50	1.7	5	#3
0.20	194 K	0.99	1.82	0.6	20	#4
0.45	RT	3.408	0.98	2.1	8	#1
0.45	194 K	3.362	n/a	2.1	n/a	#2

Table 7.1: The defect densities evaluated from DSC plots

Dislocation Densities & Crystallite Sizes

In addition to fig. 6.2, typical evolutions of the dislocation density during isochronal annealing, measured by XLPa, are presented in figs. 6.3 and 6.4. With all samples which have been HPT processed, the HPT strain amounted to a von-Mises equivalent strain of $\epsilon_{vM} = 116$. While fig. 6.3 shows isochrones of samples with different HPT processing temperature, both for samples hydrogenated by $H/Pd = 0.0075$, fig. 6.4 presents isochrones of samples after HPT-processing at RT after being hydrogenated with different H/Pd ratios. The characteristics of non-hydrogenated samples (dark green dashed line) processed under the same conditions has been added to both figures and can thus serve as a reference.

The values of the change in dislocation density $\Delta\rho$ during isochronal annealing are summarized in table 7.2 .

H/Pd	T_{deform}	$\Delta\rho$ [$10^{15}m^{-2}$]	sample identifier
0.0025	RT	2.7 ± 0.4	#7
0.0025	194 K	2.5 ± 0.4	#10
0.0075	RT	2.5 ± 0.3	#5
0.0075	194 K	2.6 ± 0.2	#9
0.20	RT	3.2 ± 0.3	#3
0.20	194 K	3.6 ± 0.4	#4
0.45	RT	2.3 ± 0.3	#1
0.45	194 K	3.1 ± 0.2	#2

Table 7.2: The dislocation densities evaluated from XLPa

As a first conclusion from the values shown in table 7.2, it turns out that the deformation temperature has no significant impact on the dislocation density; the curves are identical within the measurement accuracy.

The hydrogenated samples show the trend already indicated by the vacancy concentrations resulting from DSC: there is a slight tendency to higher dislocation densities for increasing H content. As in case of the sample with $H/Pd = 0.45$ shown in fig. 7.1 (c), these values are constant during isochronal annealing up to a homologous temperature of $T = 0.32T_m = 300^\circ C$, i.e. during stage III, but decrease beyond that temperature, i.e. during stage IV.

The dislocation density of the non-hydrogenated sample is decreasing steadily from the beginning, i.e. already in stage III. Therefore, the dislocations in the hydrogenated samples can be considered as stabilized by solute H, in some analogous way as the vacancy annealing gets stabilized as described before.

With the XLPA method, in parallel to the dislocation density, ρ , the crystallite size, D , could be evaluated (cf. figs 6.5 and 6.6). The obtained isochrones show no change of crystallite size from RT to 400°C , i.e. during stages III and IV, and the Pd-H samples even no change beyond 400°C . When comparing these results with the evolutions of dislocation density demonstrated in figs. 7.1, 6.3 and 6.4, it can be concluded that in case of the non-hydrogenated HPT processed samples all the deformation-induced dislocations are part of subgrain (crystallite) boundaries which disappear at the same annealing temperature whereas in case of the hydrogenated samples, only dislocations from the grain interior anneal while those of subgrain boundaries remain stable against even the highest annealing temperatures. Altogether, these findings prove that the presence of hydrogen prevents both the free dislocations as well as those of the subgrain boundaries from annealing, and that hydrogen acts as stabilizing atom sort for both type of defects.

The isochrones by microhardness (HV), most of them presented in figs. 6.7 and 6.8, confirm the results discussed by the example of fig. 7.1 (b); in stage III, i.e. for temperatures $T < 100^\circ\text{C}$ and especially $T < 200^\circ\text{C}$, the HPT-processed Pd-samples show anneal hardening effects. This is especially true when the Pd-sample are hydrogenated before HPT processing. Comparing the isochrones with different H contents being present before HPT processing, a small increase of anneal hardening effect can be seen, however, the HPT processing temperature does not play a significant role. In order to find out where the anneal hardening effects come from, we discuss the concomitant changes of the densities of deformation-induced defects, i.e. dislocations, crystallite size and vacancy-type defects.

In stage IV, i.e. at annealing temperatures $200^\circ\text{C} \lesssim T \lesssim 310^\circ\text{C}$, the dislocation density is more or less constant, irrespective of deformation temperature and especially of the H-content (compare figs 6.3, 6.4 of dislocation density variation with figs. 6.7, 6.8 and 6.9 of HV variation). Within the same temperature interval, also the crystallite size (figs. 6.5 and 6.6) is roughly constant. Therefore the strong decrease of HV in this interval of annealing temperatures can be only explained with the coarsening and the annealing of vacancy agglomerates. This is also in agreement with the findings in literature identifying stage IV of annealing with the that of vacancy agglomerates. At the final part of stage IV, beyond the annealing temperature $310^\circ\text{C} \lesssim T \lesssim 400^\circ\text{C}$, however, the dislocation density shows a slight decrease (figs. 6.3 and 6.4), which suggests to be responsible for the further decrease of HV in this temperature interval. A sharper decrease of microhardness is observed beyond temperatures $T > 400^\circ\text{C}$, which conforms with another (although slighter) decrease of dislocation density, but also with an increase of the crystallite size. Those simultaneous processes indicate that the annealing

dislocations are part of the crystallite boundaries, while those which already annealed in stage IV were part of the crystallite interiors. Therefore, in agreement with literature (e.g. [45], see also chapters 1 and 2), the annealing stage observed beyond temperatures $T > 400^\circ\text{C}$ corresponds to stage V of the annealing characteristics of plastically deformed materials, also called "primary recrystallization", while stage IV is essentially a "recovery" stage with annealing of free defects.

Fig. 6.8 shows a comparison of isochrones by microhardness for samples with different deformation temperatures and the same von Mises strain, ϵ_{vM} . The differences in microhardness were almost within the measuring error; they suggest that also the defect densities both those of vacancy type defects as well as those of dislocations were not too different. That result was found for all four different H concentrations similarly; it can be understood by the fact that the differences in T_{deform} being about 100 K are not too large, i.e. $0.1T_m < T_{deform} < 0.2T_m$.

The dependences of isochronal values of microhardness on different initial H-concentrations are depicted in fig. 6.9. Similarly to the characteristics of dislocation and crystallite size isochrones, they are shifted with their annealing stages to higher annealing temperatures when the materials have been doped with hydrogen. The shift is a maximum between the material without hydrogen and the materials with any hydrogen present before HPT deformation; further increase of the H content, however, has much less or no effect to the temperatures of anneal maxima. Compared to the characteristics of vacancy and dislocation densities, and crystallite size variations, the temperature of the first annealing stage of the non-hydrogenated materials well coincides with the first decrease of dislocation density; in the hydrogenated materials, however, the analogous decrease already occur in parallel to the annealing of vacancy defects. This suggests - indirectly - that in Pd-materials without H being present, no or at least much less vacancy defects have been generated/stored in the sample, as it is described by the defectant model of Kirchheim [20][21] described in sections 4.2 and 1.2.

Concerning the effect of the initial H concentration to the extent of microhardness, the results are analogous to the peak shift effect described above: while the first few percent of hydrogenation have a strong impact to the microhardness including the formation of a relative hardness peak, the addition of further hydrogen does not much change it.

The appearance of a relative hardness peak itself is another hint to the formation of vacancy agglomerates; as already mentioned before, vacancy agglomeration is the only process during annealing treatment which can cause an increase of strength (hardness) [61] ; e.g. the rearrangement or annealing

of dislocations always leads to a decrease of strength (hardness). - The hardness isochrones are consistent with the DSC plots of differently hydrogenated materials, see fig. 6.2 ; hydrogen doping induces a stabilization of HPT-induced defects. Again, the difference to the non-hydrogenated material is a maximum while the content of hydrogen H/Pd among the hydrogenated materials does not matter too much, assumed a threshold value in the order of magnitude of a few percent is surpassed.

Quantitative Estimations of Hardness Contribution

The discussion of the isochrones of both the non-hydrogenated and the hydrogenated HPT-processed materials exhibited the following three annealing stages: - stage III with the formation of vacancy agglomerates showing anneal hardening, stage IV comprising the coarsening and dissolution of vacancy agglomerates causing anneal softening, and at the same time the annealing of dislocations from subgrain interiors, and stage V being another softening stage which exhibits subgrain/crystallite coarsening while dislocations from grain boundaries anneal. In order to substantiate those interpretations, the three stages III, IV and V are considered quantitatively with respect to their specific increase or decrease of hardness, on the basis of equations 4.5, 4.6, 4.7, 4.10 and 4.12 introduced in ch. 4.3 and by means of the different defect densities measured by XLPA and DSC.

Table 7.3 summarizes all changes of macroscopic strength values, separated by the three annealing stages III, IV, V. For each annealing stage, in series the measured hardness difference, the corresponding difference of resolved shear stresses, and finally the differences of shear stresses calculated by means of eqs.4.5, 4.6, 4.7, 4.10 and 4.12 are presented. All samples were deformed up to a von-Mises equivalent strain of $\epsilon_{vM} = 116$ at two different deformation temperatures, T_{deform} . Data for Pd pure materials and materials with four different H concentrations, H/Pd, being present before HPT are included. For all materials, the initial strength of the defect-free metal is $\tau_0 = 55MPa$ as calculated from the initial hardness of a well annealed Pd (cf. table 1.1 and eq. 4.12). For the choice of other constants and parameters (e.g. dislocation configuration parameter α , Burgers vector of vacancy loops) see chapter 4.3.

Comparing now the experimental results of hardness variations with those of the calculated ones, it can be seen that in general the deviations between experiment and modelling remain within $\pm 20\%$; we can thus conclude that the interpretation of annealing stages is correct within these limits. The deviations come from uncertainties in the choice of parameters and constants, e.g. the dependence of shear modulus on the H-content, the partial overlap of defect annealing between the annealing stages, etc.. Systematic

	H/Pd	0.45	0.45	0.20	0.20	0.0075	0.0025	0.0075	0.0025	without H
	T _{deform} [K]	296	194	296	194	296	296	194	194	296
<u>annealing stages III - IV increase</u> (Vacancy-agglomerate formation) @ T ≈ 200°C	ΔHV (exp.) [MPa]	320	210	400	350	130	470	230	230	50
	Δτ (exp.) [MPa] eq. 4.12	35	23	44	38	14	51	25	25	5
	Δτ (calc.) [MPa] eq. 4.6	53	49	41	41	28	67	34	38	6
<u>annealing stage IV</u> (Vacancy-agglomerates) @ 200°C < T < 300°C	ΔHV (exp.) [MPa]	-1470	-1400	-1330	-1400	-1240	-1280	-700	-1460	-912
	Δτ (exp.) [MPa] eq. 4.12	-159	-151	-144	-151	-134	-138	-76	-158	-99
	Δτ (calc.) [MPa] eq. 4.6	-206	-206	-188	-118	-132	-141	-141	-215	-55
<u>annealing stage IV</u> (free dislocations) @ 300°C < T < 420°C	ΔHV (exp) [MPa]	-350	-360	-590	-300	0	-330	-50	-110	-348
	Δτ (exp) [MPa] eq. 4.12	-38	-39	-64	-32	0	-36	-5	-12	-38
	Δτ (calc.) [MPa] eq. 4.5	-35	-54	-50	-48	-52	-35	-54	-43	-54
<u>annealing stage V</u> (dislocations of subgrain boundaries) @ T > 420°C	ΔHV (exp.) [MPa]	-200	-100	-190	-240	-100	-110	-20	-140	-20
	Δτ (exp.) [MPa] eq. 4.12	-22	-11	-21	-26	-11	-12	-2	-15	-2
	Δτ (calc.) [MPa] eq. 4.5	-35	-27	-28	-26	-24	-27	-23	-24	-31
	sample number	#1	#2	#3	#4	#5	#7	#9	#10	#11

Table 7.3: Overview of macroscopic strength values obtained from HPT- processed Pd-H

deviations can be seen only in case of annealing stage III and stage IV at lower annealing temperatures where in most cases the calculated increase of strength exceeds that of measured one. This discrepancy may arise from the fact that in most cases not all vacancies produced in HPT processing form loops/agglomerates.

Latest on basis of the quantitative calculations of stage specific hardening variations presented and compared to the experimental ones in table 7.3, one can conclude that **(i) the presence of H in the Pd-materials traps and/or stabilizes a substantial density of vacancies and vacancy agglomerates, and that (ii) they achieve as much as about 2/3 of the total strength of the material. In contrast to the vacancy-type defects, one further recognizes that (iii) the presence of H does neither affect the dislocation density nor the hardening which is caused by them.**

7.1.2 CR processed state

Common qualitative discussion of results

In comparison to HPT-processed Pd-H the results of the CR processed ones presented in fig. 7.2 are more difficult to understand. Here the H - concentration was varied while the processing temperature was kept constant, i.e. RT. For a non-hydrogenated Pd cold-rolled up to about 50 % of the initial thickness resulting in a von-Mises equivalent strain of $\epsilon_{vM} = 0.8$ (blue line), a tiny exothermic peak around $T = 124^\circ\text{C}$ appears which corresponds to the annealing of single vacancies [12] [57], as it has been the case with HPT processed Pd (H) samples. Then a distinct exothermic peak at $T = 283^\circ\text{C} = 0.30T_m$ can be observed in the DSC plot, fig. 7.2(a). For Pd-H with H/Pd = 0.45 with about the same CR deformation degree (red line), this distinct peak is split into two peaks at $T = 282^\circ\text{C} = 0.30T_m$ and at $T = 301^\circ\text{C} = 0.31T_m$, respectively. The trend of splitting into two exothermic peaks is even more pronounced with a H concentration of H/Pd = 0.0075 and strain $\epsilon_{vM} = 0.73$ (green line); these peaks occur at $T = 281^\circ\text{C} = 0.30T_m$ and at $T = 329^\circ\text{C} = 0.33T_m$, respectively.

For the same reasons as described above for the case of HPT-processed Pd, these splitted peaks have to be ascribed to the annealing of vacancy-type defects [12][57][59] : the corresponding dislocation density, fig. 7.2 (c), is fairly constant within the measuring accuracy at least below $T = 300^\circ\text{C} = 0.31T_m$. The same finding is true for the crystallite size, fig. 7.2 (d), till about the same annealing temperature. Both results suggest to identify the observed

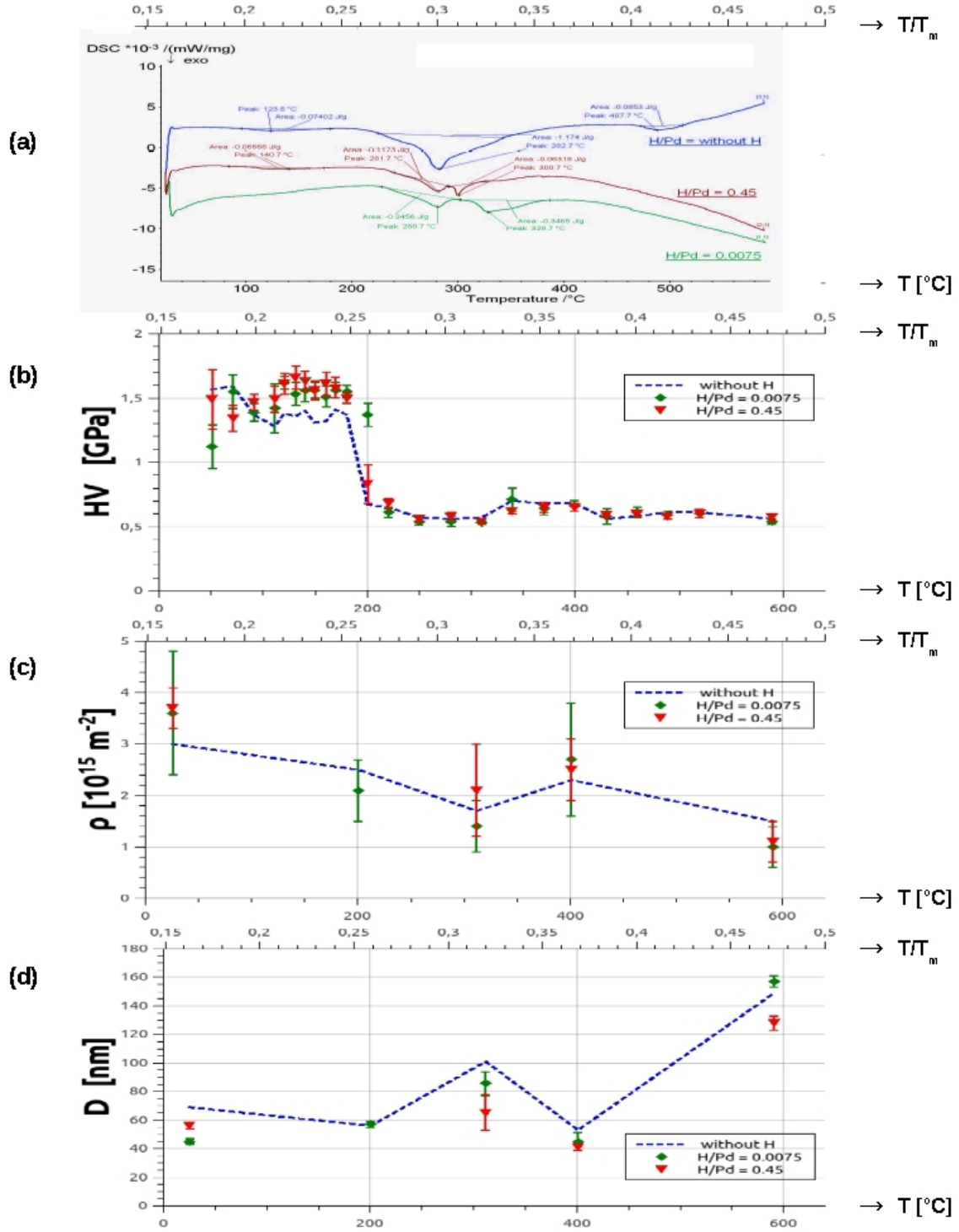


Figure 7.2: Correlated isochrones of Pd-H **deformed via CR** with different H/Pd ratios, i.e. (a) DSC plot, (b) microhardness HV, (c) dislocation density ρ and (d) crystallite size D. (a): H/Pd = 0.0075 (—), H/Pd = 0.45 (—), without H (—); (b), (c), (d): H/Pd = 0.0075 (◆), H/Pd = 0.45 (▲), deformed without H (—)

DSC peaks with annealing of vacancy agglomerates. At about the same temperature and/or below it, fig 7.2 (b) shows a strong loss in hardness which again can neither be explained by the slight changes in dislocation density nor in crystallite size. Moreover, before the strong decrease, the hardness even increases which can only occur due to agglomeration of vacancies rather than due to rearrangements of dislocations.

Beyond $T \approx 400^\circ\text{C} = 0.37T_m$, the dislocation density, fig. 7.2 (c) shows a slight decrease while the crystallite size, fig. 7.2 (d), markedly increases. This means that - as in case of HPT processed Pd-H samples - stage V of annealing takes place here representing the process of primary recrystallization when the dislocations anneal out as part of the crystallite boundaries.

Within the following three sections, the annealing peaks are quantitatively evaluated with regard to their underlying annealing defects, and with regard of the quantitative correlation of these defects with the effects of hardening and softening observed.

Vacancy Concentration

Fig. 6.10 (in the previous chapter) visualizes a DSC plot of the non-hydrogenated sample cold rolled up to a von Mises equivalent strain of $\epsilon_{vM} \approx 0.75$. As already mentioned before, at first there appears a tiny exothermic peak at $T = 124^\circ\text{C}$ representing the annealing of single vacancies, with a concentration $c_{vac} = 4.5 \times 10^{-5}$ [12][57], according to eq. 5.7 using $\Delta H_v^f = 1.85 \pm 0.01$ eV/vacancy [45][59], $M = 106.42 \times 10^{-3} \text{ kg mol}^{-1}$. The second, middle exothermic peak which again evolves at $T = 283^\circ\text{C} = 0.31T_m$, refers to the annealing of vacancy agglomerates [12][57][59], as already argued in the previous section. It reveals a stored energy $E_{vac} = 1.174 \text{ J/g}$; using eq.5.7, this corresponds to a vacancy concentration of $c_{vac} = 7.2 \times 10^{-4}$. This value is about one order of magnitude larger than the concentration of single vacancies in the previous peak. The third exothermic peak which appears at $T = 488^\circ\text{C} = 0.42T_m$ exhibits a stored energy of $E_{stor} = 0.085 \text{ J/g}$. According to the previous section, it is characteristic of the annealing of dislocations [12][57][59] with a dislocation density of $\rho = 0.7 \times 10^{15} \text{ m}^{-2}$, according to eq. 5.6.

In the same DSC plot, fig. 6.10, also graphs of hydrogenated samples with an initial H concentrations of $\text{H/Pd} = 0.0075$ and cold-rolled to $\epsilon_{vM} = 0.75$ are visualized. One can see that the exothermic peaks referring to single vacancies as well as to dislocations have almost disappeared; both were near the accuracy of the used DSC equipment. In addition, as already mentioned, the

splitting of middle peak into two separate indicates the annealing of vacancy agglomerates, with two maxima in their size distribution; this fact suggest to add the vacancy concentrations evaluated from each peak to a total one, according to $c_{Vac}^{total} = (1.5 + 2.1) \times 10^{-4} = 3.6 \times 10^{-4}$.

Dislocation Densities & Crystallite Sizes

Due to XLPA analysis of the isochrone of dislocation density, fig. 6.11, the slight decrease at the beginning corresponds to a decrease of dislocation density of $\Delta\rho \approx 1.6 \times 10^{15}m^{-2}$ in the temperature range from $T = 0.16T_m$ to $T = 0.32T_m$. This slight decrease is far too small to explain the strong decrease of microhardness/strength as estimated in the next section. Because there is also no change of crystallite size within this temperature interval, fig. 6.12, the decrease of microhardness/strength must be ascribed to the annealing of vacancy agglomerates.

At higher annealing temperatures, an increase in dislocation density, fig. 6.11, ($\Delta\rho \approx 0.5 \times 10^{15}m^{-2}$) was observed in the temperature interval from $T = 0.32T_m$ to $T = 0.37T_m$ which occurs in both non-hydrogenated as well as hydrogenated deformed samples. In parallel, the crystallite size, fig. 6.12, is decreasing by $\Delta D = 35nm$. The fact that this decrease occurs at the same temperature at which the increase of dislocation density takes place, confirms the conclusions that (i) these effects are real and no artefacts and that (ii) the density changes concern dislocations which are part of the crystallite boundary. It seems that new small crystallites are formed, but why the dislocation density increases at the same time cannot be easily explained. At the subsequent temperature interval, the crystallite boundary disappears, the crystallite size D is increasing and in parallel the dislocation density ρ is again decreasing. A final observation about the variations of dislocation density and crystallite size as function of the H-content being present before CR deformation is that generally the H-content has no strong effect on the variations of these quantities. In order to see at least the trends of H-doping, all these variations are demonstrated together in table 7.4.

The evaluation procedures were the same as described in the beforehand chapter in detail for HPT-processed Pd-H using the identical parameters. c_{vac} was taken from the DSC results while $\Delta\rho$ and D were obtained from XLPA data. Compared with the non-hydrogenated sample, the vacancy concentration is almost a factor 2 smaller at the smallest content of H investigated, and even decreases by another 60% when the α' -phase of Pd-H is reached. In contrast, the dislocation densities are slightly increased when deforming weakly doped Pd-H instead of pure Pd; however further increase

of the H-content before CR has no further increasing effect to the dislocation density.

sample number	# 1	# 2	# 3
H/Pd	without	0.0075	0.45
$c_{Vac} [10^{-4}]$	7.6	$(1.5 + 2.1) = 3.6$	$(0.69 + 0.39) = 1.1$
$\Delta\rho [10^{15}m^{-2}]$	1.5	2.6	2.6
D [nm] ($T \lesssim 0.37T_m$)	~ 69	~ 58	~ 54

Table 7.4: Vacancy concentrations, dislocation densities and crystallite sizes for CR-processed Pd-H

Quantitative Estimations of Hardness Contribution

After the above qualitative discussion on the lattice defects, now some quantitative estimations follow.

Using the vacancy concentrations, dislocation densities and crystallite sizes given in table 7.4. which have been derived from DSC and XLPA, one can calculate the macroscopic strength values for each of the defects separately, by applying the same evaluation procedure as done for the HPT-processed Pd: for example, τ_0 was calculated via table 1.1; $b_{loop} = 1.1nm$ was assumed for the loops' Burgers vector, and $2R = 13 nm$ for their diameter (cf. eq. 4.6). With those data a vacancy loop density was calculated via eq. 4.7, serving now as the basis for the calculation of strength effects due to loop annealing. For the subgrain (SB) size effects, $K_y = 1 GPa nm$ was used for the Hall-Petch hardening etc.. Table 7.5 presents all the strength values calculated by means of the equations indicated. The agreement of the calculated data with the measured ones is satisfying, thus confirming both the hardening processes suggested as well as the types of the defects involved.

Comparing the (measured) contributions of different defects to total hardening, that of the vacancy agglomerates is about twice the one arising from dislocations; this ratio is about the same for the hydrogenated states. The contribution to the macroscopic strength of subgrain boundaries is small even if the crystallite size increases significantly for $T \gtrsim 0.37T_m$, i.e. in stage V. At last, one can calculate the sum of the different strength contributions via eq. 4.11 (not shown in table 7.5). It roughly combines with the experimental values derived from the microhardness measurements.

As concerns the effect of hydrogenation on the strength itself, there is an effect of about 10% for the low hydrogen content for vacancy agglomerates as well as dislocations; it can be - as in case of vacancy agglomerates - be only

	H/Pd	without H	0.0075	0.45
	HV ₀ [MPa]	523	532	496
	τ_0 (exp.) [MPa] acc. to eq. 4.12	57	58	54
	τ_0 (calc.) [MPa]	55	55	55
<u>annealing stage III</u> (Vacancy-agglomerates) @ T $\approx$ 200°C	Δ HV (exp.) [Mpa]	-899	-946	-854
	$\Delta\tau_{\text{vac}}$ (exp.) [MPa] acc. to eq. 4.12	-98	-103	-93
	$\Delta\tau_{\text{vac}}$ (calc.) [MPa] acc. to eq. 4.6	-94	-105	-98
<u>annealing stage IV</u> (dislocations) @ T $\approx$ 400°C	Δ HV _{dis} (exp.) [MPa]	-303	-422	-459
	$\Delta\tau_{\text{dis}}$ (exp.) [MPa] acc. to eq. 4.12	-33	-46	-50
	$\Delta\tau_{\text{dis}}$ (calc.) [MPa] acc. to eq. 4.5	-45	-59	-59
	HV _{SB} = const. (exp.) [MPa]	119	165	174
	τ_{SB} = const. (exp.) [MPa] acc. to eq. 4.12	13	18	19
	τ_{SB} = const. (calc.) [MPa] acc. to eq. 4.9	15	17	19
<u>annealing stage V</u>	Δ HV _{SB} (exp.) [MPa]	-83	-73	-101
	$\Delta\tau_{\text{SB}}$ (exp.) [MPa] acc. to eq. 4.12	-9	-8	-11
	$\Delta\tau_{\text{SB}}$ (calc.) [MPa] acc. to eq. 4.9	-10	-9	-11
	sample number	#1	#2	#3

Table 7.5: Macroscopic strength values for CR-deformed Pd-H

5% with the highest hydrogen content; the effect is in line with the defect concentrations measured and may result from the transition from the α - to the α' -phase occurring at about H/Pd = 0.018 (cf. fig. 1.1).

7.1.3 Comparing results of CR-processed materials with those of HPT-processing; Conclusions

The comparison of CR-processed Pd-materials with the HPT-processed ones is best done by the graphs demonstrated in figs. 7.3 and 7.4. In fig. 7.3, for the case of the non-hydrogenated Pd samples before thermal treatment, the microhardness is about 20% lower, because of the much smaller density of deformation-induced defects in the CR-processed samples which arises from the much lower von-Mises equivalent strain $\epsilon_{vM} = 0.75$ in CR, compared to $\epsilon_{vM} = 116$ in HPT.

In case of hydrogenated samples, however, the difference between CR and HPT is about 60% because of the higher difference in the density of gener-

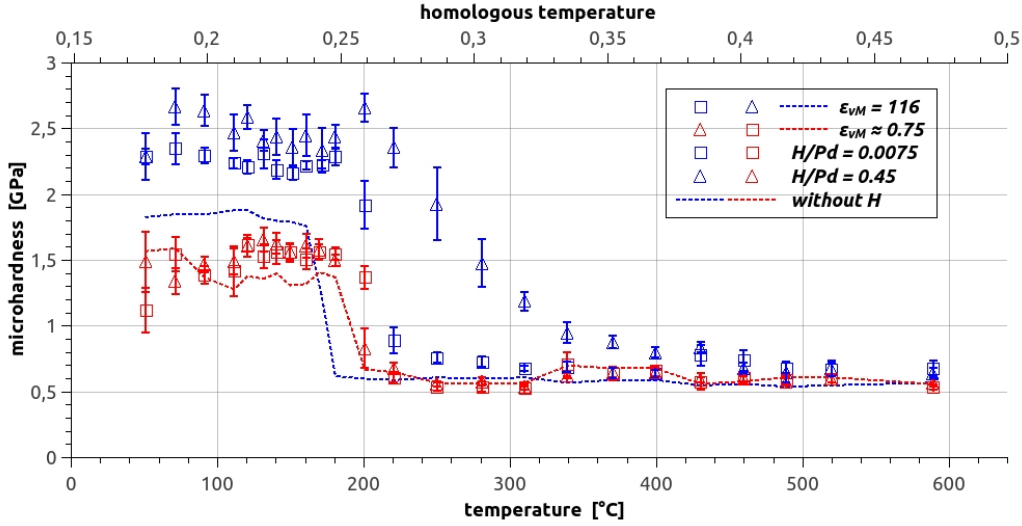


Figure 7.3: Comparison of isochrones of **microhardness** obtained by HPT and CR deformation of Pd-H, respectively. Blue symbols: deformation via HPT; red symbols: deformation via CR; squares: deformed samples charged with H/Pd = 0.0075; triangles: deformed samples charged with H/Pd = 0.45; dashed lines: deformed samples without H

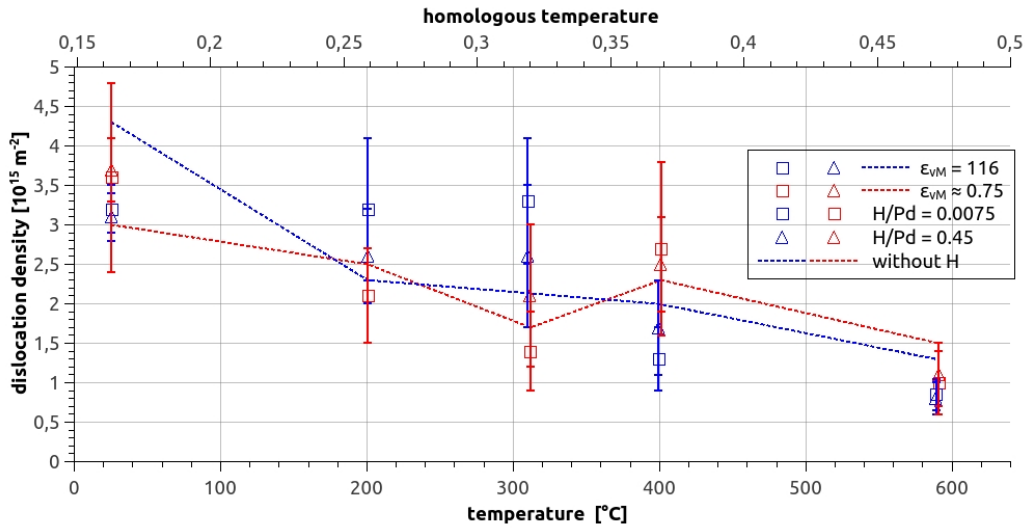


Figure 7.4: Comparison of isochrones of **dislocation density** gathered by CR and HPT deformation of Pd-H, respectively. Red symbols: deformation via CR; blue symbols: deformation via HPT; squares: deformed samples charged with H/Pd = 0.0075; triangles: deformed samples charged with H/Pd = 0.45; dashed lines: deformed samples without H

ated vacancy agglomerates caused by the presence of hydrogen: According to the results given in the two sections before, c_{Vac} is about one order of magnitude larger in the case of HPT-processed hydrogenated samples than in the case of CR-deformed ones (cf. Tables 7.1 & 7.4). The **absolute** hydrogen content only plays a minor role for both the defect densities and thus for the microhardness, too; again, in some cases, the hydrogen in the α -phase showed a higher defect trapping potential than in the α' -phase.

The strong decreases in both microhardness isochrones, i.e. that of CR- as well as of HPT-processed samples, can be clearly related to the coarsening and annealing of vacancy agglomerates, and not to the annealing of dislocations, see fig. 7.3 because the density of the latter is more or less constant till $T = 300^\circ C$.

In addition, the vacancy agglomerates found in HPT-processed hydrogenated samples are more stable since they anneal at higher homologous temperatures; this hints at the fact that the higher concentration of vacancies may result not only in more but also in larger agglomerates than in case of the CR-samples.

From fig. 7.4 it can be seen that the **dislocation densities produced by CR and HPT lie within about the same order of magnitude** resulting in roughly similar $\Delta\tau_{Dis}$, around -40 MPa. The degree/mode of deformation has only little influence to the dislocation density, although the presence of hydrogen affects the annealing behavior, i.e. it increases the annealing resistance of the dislocations. Both issues also govern the strength of materials during isochronal annealing.

Concerning the crystallite sizes (no figure), they also are within in the same order of magnitude for both deformation methods, so that also the grain size-specific softening/hardening of the two deformation types applied are similar $\Delta\tau_{SB}(HPT) \sim \Delta\tau_{SB}(CR)$. Like in case of dislocations, the impact of crystallite size differences both the deformation induced ones as well as those from different hydrogen contents are below 10%.

The results of this work received for the Pd-H system favouring the vacancy agglomerates as preferred traps for the hydrogen can be backed by the related literature work as follows:

Since the works of Alefeld [2][3] and Fukai [5] it is well known that the solute H in Pd tends to join vacancies both via their dilatational strain and their core area; the solute H accumulates within vacancies once they are generated, e.g. by plastic deformation as in the here presented case. This way, at the same time, the solute H stabilizes single vacancies during plastic deformation, and enhances the formation of vacancy agglomerates trapped to the H-atom. Depending on the type and extent of plastic deformation applied, the vacancy concentration varies and e.g. is smaller in the case of

CR than in case of HPT. Dislocations, in comparison with vacancies, have a smaller specific (=per atom) strain field and especially a smaller core so that trapping of solute H by dislocations is less probable than by vacancies. When dislocations get part of a subgrain boundary, their long-range strain fields are even getting cancelled mutually which further reduces the trapping potential by H [3]; **this is in agreement with the experimental findings for both CR- and HPT-processed materials: no stabilization of deformation-induced subgrain boundaries due to hydrogenation was observed.**

The results of the investigations of CR- and HPT processed Pd-H materials is well in line with Kirchheim's defactant concept (cf. [20] [21] and chapter 4.2). However, in the present work no evidence of the highly increased dislocation density in CR- processed Pd-H as reported by Chen et al. in 2013 [13] was found. Also a more recent paper by Chen et al. published in 2015 [37] reported hardening mechanisms and defects involved which were quite different from those found in the present work; however, Chen's deformations were done as tensile tests in-situ in the electrolyte which directly provided the hydrogen for the samples being deformed under load. In our case, all the interstitial hydrogen was removed before all measurements; so the two experiments cannot be compared directly.

7.2 Fe-C

7.2.1 HPT-processed state

Like in the discussion on Pd-H, here the results of HPT-processed samples will be considered. HPT-processing with respect to Fe-C and pure Fe, however, means consolidation and simultaneous HPT-deformation of ball milled powders of Fe0.8wt%C and pure Fe, respectively. HPT-consolidation/deformation was performed under two different pressures till deformations up to three different strains (cf. table 5.3).

Common qualitative discussion of results

Fig. 7.5 shows the isochrones received from pure Fe and Fe-C, both consolidated at $p = 6$ GPa and subsequently HPT-deformed up to a von-Mises equivalent strain of $\epsilon_{vM} = 83$. Isochrones of stored energy (DSC), microhardness (HV), dislocation density (XLPD) and crystallite size (XLPD) were recorded. In fig. 7.5 (a) the DSC plots exhibit two small exothermic peaks

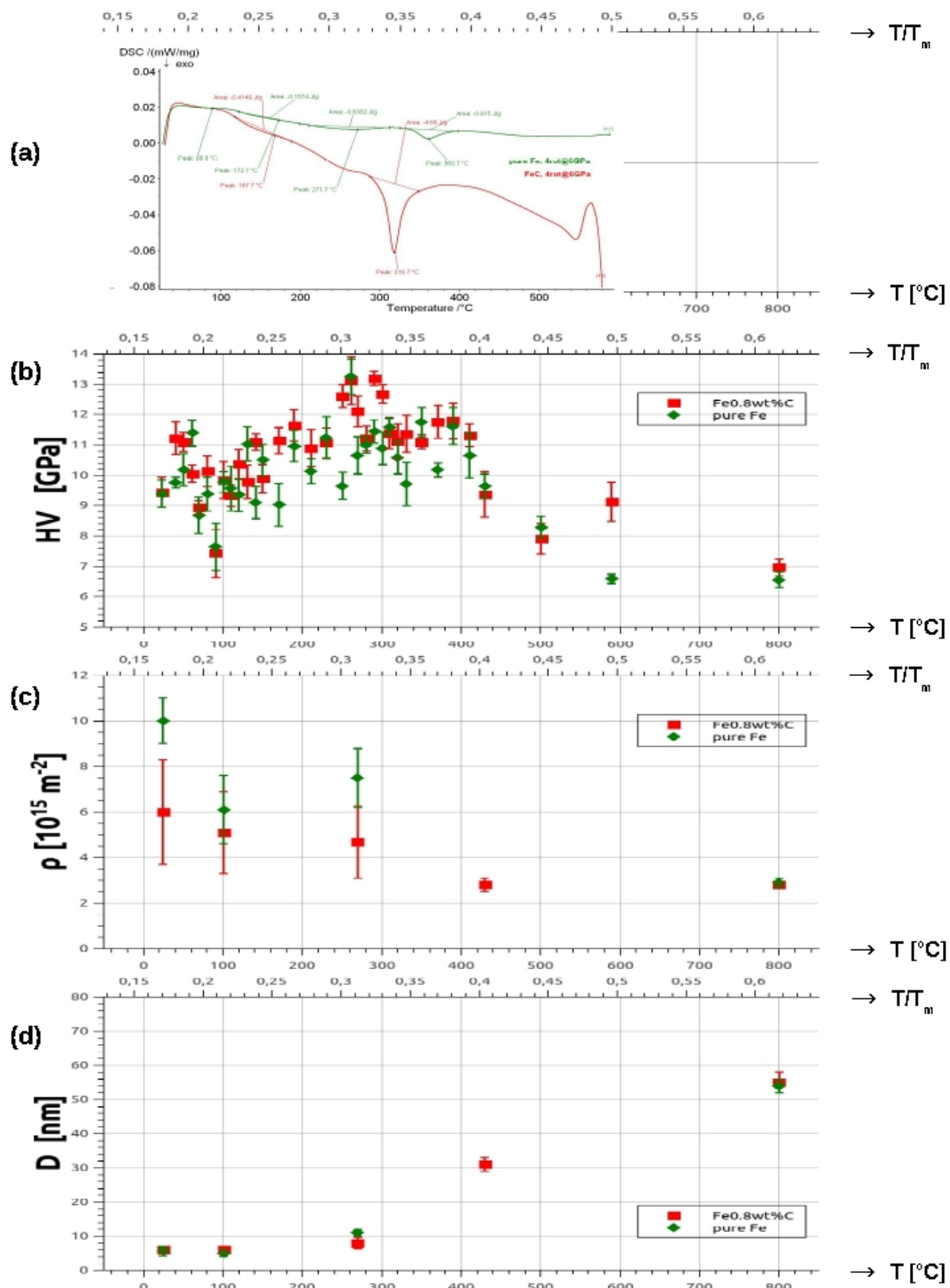


Figure 7.5: Comparison of isochrones of pure Fe (green) and Fe-0.8wt% C (red) after HPT-processing at 6 GPa and RT with 4 rotations achieving $\epsilon_{VM} = 83$. Isochrones denote the variations of (a) stored energy (DSC), (b) microhardness HV, (c) dislocation density ρ (XLP) and (c) crystallite size D (XLP)

at about $T = 170^\circ\text{C} = 0.25T_m$ and $T = 270^\circ\text{C} = 0.31T_m$, respectively. In addition, a larger exothermic peak at $T = 310\ldots360^\circ\text{C} = 0.34\ldots0.36T_m$ was found. According to literature [12][57][61], the first peak should represent the annealing of single vacancies (stage III as mentioned in the introduction section), while the second one stands for the annealing of vacancy agglomerates (stage IV). The third peak (annealing stage V), in turn, should represent the annealing of dislocations.

When comparing the other isochrones i.e. that of microhardness, dislocation density and subgrain size, the hypothesis that peaks 1 and 2 reflect the annealing of single vacancies and vacancy agglomerates, respectively, is confirmed by the following facts: (i) the hardness increases during the stages III and IV while it decreases in stage V, and at the same time (ii) the dislocation density is constant (stages III and IV) or even decreases (stage V); if thermally activated dislocation rearrangements occur in stages III and/or IV with the same dislocation density, they never would achieve a hardening but the same or a lower strength.

Moreover, with the same HPT processing values, the DSC peak 3 is larger in case of Fe-C than of Fe (Fig. 7.5 (a)), as it is with the hardness values. Comparing the dislocation density and subgrain size characteristics during isochronal annealing, however, one finds that the dislocation density is **smaller** with Fe-C than with Fe so that there is obviously no trapping effect of dislocations by the C-atoms; this again confirms the above conclusion that the increased isochronal hardening in Fe-C cannot result from dislocations i.e. dislocation hardening but from hardening through vacancy agglomerates.

The decrease of dislocation density starts at about 300°C where the hardness is still increasing. That means that hardening by vacancy agglomerates and softening by dislocations and/or subgrain growth occur simultaneously. Therefore a reliable interpretation only seems possible if the individual densities of these three defect types can be determined separately; then a quantitative estimation of the different hardening contributions would be possible, and a comparison with the total hardness variations observed, too. This attempt is done in the next sections.

Vacancy Concentration and Dislocation Density

For a quantitative evaluation of HPT-induced defect densities, the results from DSC and XLPA measurements presented in figs. 6.14, 6.15 and 6.16 concerning all the HPT-processed samples out of (a) Fe 0.8wt% C and (b) pure Fe with different pressures and von-Mises equivalent strains were used,

and inserted in eq. 5.7. For the formation energy of single vacancy, that of pure Fe $\Delta H_v^f = 1.4 \text{ eV}$ was used as well as $M = 55.85 \times 10^{-3} \text{ kg mol}^{-1}$ (cf. Table 1.2) for the molar mass. For Fe 0.8wt%C the same values were taken as well since more reliable values were not available.

As already mentioned, a significant overlap of annealing peaks occurs in stage IV. Intending the separation of the annealing peak of vacancy agglomerates from that of dislocations, the procedure used by Setman et al [57] was chosen: at first, the stored energy of dislocations $E_{stor}(dis)$ was calculated from their density measured by XLPA, $\Delta\rho_{Dis}$ (eq. 5.6). The difference between stage V's total peak area measured by DSC i.e. E_{stor} , and the value $E_{stor}(dis)$ calculated from $\Delta\rho_{Dis}$ resulting from XLPA, is being attributed to the annealing of vacancy agglomerates.

Table 7.6 summarizes the evaluated concentrations of single vacancies, va-

	sample name	FeC_10rot _3.8GPa	FeC_20rot _4GPa	FeC_4rot _6GPa	Fe_10rot _6GPa	Fe_4rot _6GPa
	C content [wt%]	0.8	0.8	0.8	without	without
	ϵ_{vM}	207	414	83	207	83
	p_{HPT} [GPa]	~ 4	4	6	6	6
<u>annealing stage III</u> (single vacancy) @ $T \approx 160^\circ\text{C}$	$c_{vac} [10^{-4}]$	2.5	1.5	1.7	0.7	2.3
<u>annealing stage IV</u> (vacancy agglomerates) @ $200^\circ\text{C} < T < 300^\circ\text{C}$	$c_{vac} [10^{-4}]$	36.7	41.6	14.6	17.6	7.6
<u>annealing stage V</u> (dislocations) @ $300^\circ\text{C} < T < 500^\circ\text{C}$	$\Delta\rho [10^{15}\text{m}^{-2}]$	2.9	4.2	3.2	2.7	2.5

Table 7.6: Evaluated defect densities c_{vac} and $\Delta\rho$ in pure Fe and Fe0.8wt%C

cancy agglomerates as well as the dislocation densities from DSC and XLPA, respectively. In case of pure Fe, a significant influence of the achieved strain ϵ_{vM} and/or the HPT pressure on the defect densities was found for vacancy agglomerates only. The same is true for the influence of C-content; concerning the dislocation density, higher C-concentrations of the HPT-processed samples yielded even lower dislocation densities than those of pure Fe. In Fe-C samples at the highest strains at $\epsilon_{vM} = 207$, a saturation in defect densities can be seen.

Dislocation Densities & Crystallite Sizes

XLPA investigations have been undertaken to receive quantitative information on both the dislocation density and the crystallite size, during isochronal thermal treatment in parallel to DSC and microhardness. The results are given in Figs. 6.15, 6.16 and, for comparison with the isochrones of the other properties, in Figs. 7.5 (c) and (d). The changes of dislocation density during isochronal thermal treatment are given numerically in Table 7.6 for all types of Fe/Fe-C materials and processing. As already mentioned, neither the C-content nor the HPT-parameter chosen have a significant effect to the dislocation density, except some tendency to even lower dislocation densities in case of the Fe-C materials. The most apparent feature comparing the behavior of dislocation density ρ with that of crystallite size D is the decrease of ρ and simultaneous increase of D within the temperature range 300°C - 400°C which shows that the dislocations annealing here must be part of the crystallite boundaries. At any case, this behavior of dislocations and crystallite boundaries stands in strong contrast to the behavior of HPT-induced vacancy agglomerates which significantly depend on the HPT parameter chosen and even stronger on the C-content.

Hardness Contributions and Quantitative Estimations

As the values and variations of microhardness are typical of the defect densities and/or -arrangements behind, they are an indirect but valuable tool to identify the individual lattice defects via their hardening and annealing characteristics. When considering the isochrones of microhardness in terms of C-content and different HPT parameters (Figs. 6.17, 6.18 and 7.5 (b)), one finds that the extent of hardness maximum of the Fe-C material markedly exceeds that of the pure Fe material, but that the extent does not depend on the HPT parameters chosen. When one compares this result with the measured vacancy concentrations given in Table 7.6, it is compatible with the constancy of vacancy concentrations found for the single vacancies, and also with the constancy of the measured dislocation densities, but it is not compatible with the variations of vacancy concentrations being connected with the vacancy agglomerates. The latter, however, with their size and interparticle distance, should determine the hardness. A possible explanation of this discrepancy may be that there exists a critical minimum vacancy agglomerate size: agglomerates with sizes below that critical one do not affect the hardness, like it is with single vacancies. They may develop in increasing numbers by means of increasing vacancy concentrations without relevance

for the hardness.

As in the case of HPT processed Fe-C materials, one can check now whether the measured defect-specific increases/decreases of hardness agree with those calculated from the measured defect densities, by means of the model equations 4.5, 4.6, 4.9 and 4.12 yielding defect-specific hardening contributions. The results of this check is demonstrated in Table 7.7:

Because of the hardness' independence of HPT processing parameters, for the following comparisons of experimental data with theoretical estimations the experimental hardness values of Fe- samples on the one hand, those of Fe0.8wt%C samples on the other, have been averaged. Both experimental and estimated values are summarized in table 7.7, separated by the type of each deformation-induced lattice defect type and for Fe0.8wt%C and for pure Fe, respectively.

For the theoretical estimations, two average vacancy concentrations (i.e. specific to the two different purities) were calculated from the DSC plots and the data given in table 7.6. For the Burgers vector of vacancy agglomerates, $b_{loop} = 1.0 \text{ nm}$ was assumed which is about four times the length of a Burgers vector in the bcc lattice of pure Fe and/or Fe0.8wt%C. For the transformation of hardness HV values to those of shear stresses, eq. 4.7 was used. Moreover, the initial strength of the defect-free Fe for all samples was derived from the hardness of non-processed materials (cf. table 1.2 and eq. 4.12) to be $\tau_0 = 0.70 \text{ GPa}$.

The changes in macroscopic strength due to dislocation annealing, $\Delta\tau_{Dis}$, were calculated via eq. 4.5 based on the changes in dislocation density, $\Delta\rho$, measured by XLP. For the evaluation of strength due to crystallite size, τ_{SB} , and its change due to annealing, $\Delta\tau_{SB}$, the Hall-Petch relation, eq. 4.9, was applied using a value of $K_y = 6 \text{ GPa nm}$. The experimental values for crystallite size, D, were obtained from XLP.

For $T < 0.31T_m$ i.e. $T < 300^\circ\text{C}$, the crystallite size is constant and therefore contributes with a constant offset, τ_{SB} , to the macroscopic strength. At temperatures above that temperature, the marked decrease in strength, $\Delta\tau_{SB}$, is due to both dislocation annealing and subgrain coarsening.

Let us compare now the results given in Table 7.7 of stage/defect specific experimental hardness data with the calculated ones:

First of all, all calculated strength contributions - those from changes of vacancy agglomerates, dislocations, or those from subgrain (crystallite size) - do agree with the experimental ones within about $\pm 15\%$. In view of the coarse assumptions and simplifications regarding the hardening laws, these agreements appear as very good, and confirm the said conclusions on the special defects and mechanisms operating in the different annealing stages. Secondly, according to the increase of number of vacancy agglomerates, the

	C/Fe	0.8	without
	HV ₀ (exp.) [MPa]	7340	6380
	τ_0 (exp.) [MPa] acc. to eq. 4.12	800	700
	τ_0 (calc.) [MPa]	700	700
<u>annealing stage IV</u> (vacancy-agglomerates) @ 200°C < T < 300°C	Δ HV (exp.) [MPa]	-1900	-1060
	$\Delta\tau_{\text{vac}}$ (exp.) [MPa] acc. to eq. 4.12	-210	-120
	$\Delta\tau_{\text{vac}}$ (calc.) [MPa] acc. to eq. 4.6	-280	-120
<u>annealing stage IV</u> (dislocations) @ 300°C < T < 500°C	Δ HV _{dis} (exp.) [MPa]	-3760	-2620
	$\Delta\tau_{\text{dis}}$ (exp.) [MPa] acc. to eq. 4.12	-410	-290
	$\Delta\tau_{\text{dis}}$ (calc.) [MPa] acc. to eq. 4.5	-450	-340
	HV _{SB} = const. (exp.) [MPa]	8350	8250
	τ_{SB} = const. (exp.) [MPa] acc. to eq. 4.12	910	900
	τ_{SB} = const. (calc.) [MPa] acc. to eq. 4.9	970	840
<u>annealing stage V</u> (dislocations, primary recrystall.) @ T > 300°C	Δ HV _{SB} (exp.) [MPa]	-1000	-1050
	$\Delta\tau_{\text{SB}}$ (exp.) [MPa] acc. to eq. 4.12	-110	-110
	$\Delta\tau_{\text{SB}}$ (calc.) [MPa] acc. to eq. 4.9	-100	-110

Table 7.7: Strength values for individual lattice defects achieved in HPT-processed (cf. Table 5.3) Fe0.8wt%C and pure Fe, respectively.

largest change in hardness because of the presence of the defactant C occurred with those agglomerates (factor 2), while the change in hardness from the dislocations due to the presence of C was distinctly smaller (factor 1.3 or less). As a side effect, it was found that the absolute amount of constant grain boundary strength τ_{SB} was increased by the presence of C by a factor 1.2. The coarsening of subgrain size, and/or the annealing of grain boundary dislocations, however, did not show any difference between the C-doped sample and that of pure Fe, neither what concerns the dislocation density (Table 7.6), nor regarding the change of strength, i.e. $\Delta\tau_{\text{SB}}$. (Table 7.7).

7.2.2 Ball milled state

The ball milled state is the initial state of Fe0.8wt%C and pure Fe delivered as powders. Fe powder with 99.99% purity together with graphite flake of

the same purity was ball milled for 100 h. As ball milling is a kind of plastic deformation, this status has been subject of the current work as well, not at least to find out whether this initial state affects the HPT processed one reported in the last section.

Vacancy Concentration, Dislocation Densities & Crystallite Sizes

Fig. 6.19 visualizes DSC plots of ball milled Fe0.8wt%C and of additionally HPT-processed Fe0.8wt%C up to $\epsilon_{vM} = 414$. As being typical of a plastically deformed material, not only the HPT-processed material but also the ball milled one shows exothermic peaks. As repeatedly mentioned in the hitherto discussion, the first peak refers to the annealing of single vacancies / small agglomerates while the second one reflects both the annealing of vacancy agglomerates and dislocations. It can be seen from Fig. 6.19 that the types of defects are essentially the same with the BM-samples but that their densities - because of the clearly larger DSC peak areas - are larger than those after BM + HPT processing. To get a more reliable and quantitative result, the procedure already applied to the massive Fe and Fe-C samples was followed here also: the stored energies of dislocations were calculated from the dislocation density measured by XLPA, and then subtracted from the measured peak area in the DSC measurement; the stored energy left has been attributed to that of the vacancy agglomerates and the vacancy concentrations related to them. Table 7.8 shows the results concerning the specific defect densities of the BM-samples and compares them with those of HPT already presented before.

One can see that the vacancy concentrations - both those of single vacancies as well as those of vacancy agglomerates - after BM and HPT-processing were much smaller than after BM solely. Therefore the impact of HPT to the vacancy concentration has been much stronger than that of BM; so there is no cumulative effect for the vacancy concentrations, and we can consider/compare both treatments independently. On the other hand, one is surprised on the fact that the vacancy concentrations with both the single and multiple vacancy defects are 2 ... 20 times larger after ball milling than after HPT-processing.

	Ball milled (BM)	BM + HPT processed
$c_{vac}[10^{-3}]$ (single vacancy)	3.16	0.15
$c_{vac}[10^{-3}]$ (agglomerate)	7.9	4.16
$\Delta\rho_{Dis}[10^{15}m^{-2}]$	2.3	2.9
D [nm]	5 ... 70	5 ... 70

Table 7.8: Defect densities c_{vac} , ρ_{Dis} and crystallite sizes D in ball milled and in additionally HPT-processed ($p = 4$ GPa, $\epsilon_{vM} = 414$) Fe0.8wt%C evaluated from DSC & XLP. For the values of ρ_{Dis} and crystallite sizes D , see also Fig. 6.20.

This can be understood in terms of crystallographic deformation axes and strain rates being typical of the deformation mode applied. Ball milling is a multiaxial three-dimensional plastic deformation, while torsion is a two dimensional biaxial shear deformation. While in the first mode the number of active non-planar deformation slip systems which can achieve high vacancy concentrations is very high, in the second mode this number is limited; therefore only a relatively low vacancy number can be produced. Moreover, the strain rates of ball milling are up to 5 orders of magnitude higher than that of HPT-processing [39], which induces a higher generation rate of vacancies without changing their annihilation rate, thus resulting in a higher vacancy concentration (compare the model papers [100], [101] by M. Zehetbauer et al., and the experimental paper by D. Setman et al. [102]).

The dislocation density isochrones after BM, and after BM plus HPT, respectively, can be seen from Fig. 6.20 and Table 7.8. Compared to the dislocation densities after BM solely, that of additional HPT-processing increased the dislocation density only slightly, i.e. by a factor 1.2 at maximum. The crystallite size (Fig. 6.20 and Table 7.8) of as-milled powder is largely unaffected by HPT-processing of the Fe0.8wt%C powder; it agrees well with the isochrone by crystallite size of HPT-processed Fe-C itself. In other words: already after ball milling solely, the crystallite size is constant for $T < 0.33T_m$ and is increasing for $T > 0.35T_m$, and these values do not significantly change after additional HPT processing.

7.2.3 Ball milled and/or HPT-processed Fe and Fe-C: Summary & Conclusion

By summing up the results and their discussion concerning the Fe and Fe-C materials, the following statements can be given:

1. Both the ball-milled and ball-milled plus HPT-processed samples show the annealing of single and multiple vacancies, dislocations, and also subgrain walls;
2. Ball-milling before HPT neither affects the microstructure nor the lattice defect densities achieved by HPT alone, at least for HPT deforma-

tions of $\epsilon_{vM} \gtrsim 60$;

3. The amount of HPT-deformation strongly affects the density of vacancies being part of agglomerates, by up to a factor of 3; that of single vacancies, however, is not affected at all, while that of dislocations and of subgrain boundaries are affected by far less than a factor 2 only.
4. The pressure of HPT does not have a significant influence to the density of lattice defects, but it should be as large as possible in order to receive a maximum densification when the original sample material is being consolidated from ball milled powders of pure Fe and Fe-C.
5. The presence of C increases the vacancy concentration by up to a factor 3.5;
6. Ball milling yields - compared to HPT - about a factor 10 higher vacancy concentrations as part of vacancy agglomerates, but dislocation densities and densities of subgrain boundaries are of the same order of magnitude. Both the higher strain rate as well as the higher number of slip systems activated in Ball Milling in comparison to HPT may be plausible reasons for this result.
7. Any increase of the number of vacancy agglomerates - be it from higher deformation or from C-atom content - leads to increases of the strength.
8. All measurements concerning the stabilization of defects in Fe and Fe-C are in accordance with recent ones in literature. In particular, they are fully in line with the defectant model created by R. Kirchheim [19] [20] in 2007.

Chapter 8

Final Remarks: Summary & Comparison of Systems, Outlook

8.1 Summary & Comparison of Systems

The aim of the work was to find out which and to which extent the stability of different sorts of lattice defects such as vacancies, vacancy agglomerates, dislocations, and subgrain boundaries is affected by the presence of solute elements. As model materials, the systems Pd-H and Fe-C were chosen, not at least for the sake of possible comparison with existing literature data.

To produce the lattice defects, several types of plastic deformation were chosen, those are (i) HPT as the most versatile representant of the group of SPD deformation techniques, and also (ii) Ball Milling (BM), both methods promising a maximum density of deformation induced defects. For comparison with literature, also defects from (iii) conventional Cold Rolling (CR) were investigated.

For the characterization of defects, the method of isochronal annealing plus DSC was applied, using the fact that defects with different migration enthalpy anneal at different annealing temperatures. In case of overlaps of the annealing peaks of different types of defects, additional analysis methods were applied, above all the method of X-ray Line Profile Analysis, where the broadening of the profile is only sensitive to dislocations, and to the size of subgrains, and not to vacancy type defects. Another helpful method has been that of microhardness measurement, as this method is the only mechanical one which can be used during isochronal anneals of the very same samples, and is also sensitive to the presence/density of vacancy agglomerates. By

consequent application of all these methods including sensible combinations of them it was possible to distinguish all the defects in charge and to evaluate their densities.

The results of this thesis can be summarized as follows:

In general, the trapping effects observed in both systems Pd-H and Fe-C were found to be similar:

- In both cases, from all the different deformation-induced lattice defects, mainly the vacancies have been trapped by the solute element, be it H in Pd, or C in Fe, irrespective of the extent of strains and the deformation modes applied.
- In both systems, the increase of the solute concentration H or C in Pd or Fe, led to significant increases in the concentrations of the vacancies/vacancy agglomerates: They typically amount to about 10^{-4} without solute atoms, but after adding H in Pd, or C in Fe, they can reach concentrations of several 10^{-3} depending on the deformation strain applied.
- In contrast to that, the dislocation-type defects have been trapped much less than vacancy defects or even not at all, in both systems Pd-H and Fe-C. The typical order of magnitude of dislocation density is several $10^{15}m^{-2}$. Also the number of deformation-induced subgrain (or crystallite) boundaries only slightly depends on the concentration of the solutes, i.e. shows a decrease by about 20% at maximum. The reasons may lie in the smaller specific free volume of dislocations and subgrain boundaries, compared to vacancy type defects.
- The identification of thermally driven vacancy agglomeration is suggested by the hardening observed in stage III of annealing (between $0.26T_m$ and $0.32T_m$, T_m being the melting temperature in K). There is no other defect than vacancies predestined for the hardening: neither dislocations nor subgrain boundaries would be capable to cause this anneal hardening effect;
- The experimental results obtained in both systems - Pd-H as well as Fe-C - supply/extend the knowledge about the defectants' effects on the stability of deformation induced lattice defects to higher defect densities, and they are still in consistency with the defectant concept of Kirchheim.

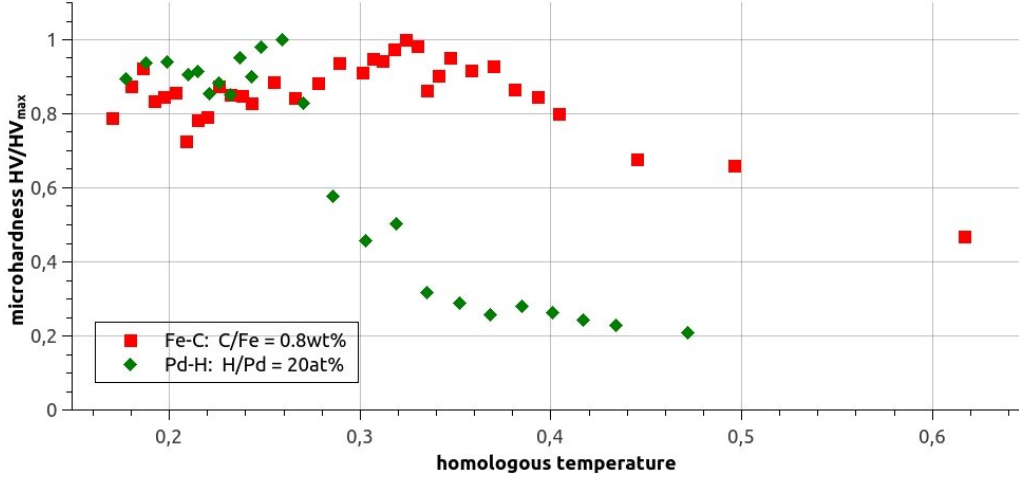


Figure 8.1: Microhardness isochrones of equally HPT-processed Pd-H (green) and Fe-C (red) materials

Differences in the effects observed in the two systems Pd-H and Fe-C only concern the thermal stability of defects. This can be recognized when doing a fair comparison of the relevant isochrones, e.g. of the sensitive microhardness isochrones as function of the homologous deformation temperatures of two equally HPT-deformed Pd-H and Fe-C materials, as shown in Fig. 8.1. While in the system Pd-H the hardness maximum due to vacancy agglomeration appears already at $T = 0.26T_m$ (T_m is the melting temperature in K), in Fe-C it only occurs beyond $T = 0.32T_m$, thus indicating a higher thermal stability of the latter system. This stability of Fe-C is higher in spite of the much larger concentration of the solute in case of Pd-H! To explain this, one should consider the differences of these two systems (i) in atomic radii ratios $r(\text{H})/r(\text{Pd}) = 0.31$ for Pd-H, and $r(\text{C})/r(\text{Fe}) = 0.43$ for Fe-C, (ii) in lattice types (fcc vs. bcc), and (iii) in the atomic mobility of H and C. From these points of view, one can qualitatively understand this difference in thermal stability.

8.2 Outlook

Although all above mentioned research questions were answered within the framework this thesis, some work has still to be done.

- (i) It is desirable to measure the size and contribution of vacancy loops

within Pd-H. Besides High-Resolution Transmission Electron Microscopy (HRTEM) which needs very extensive work, a promising alternative would be the so-called in-situ Electron Channeling Contrast Imaging (ECCI) introduced by S. Zaefferer, Max-Planck-Institut für Eisenforschung, Düsseldorf (Germany) [103] to be carried out in a FEG Scanning Electron Microscope.

(ii) Furthermore, detailed investigations on the number of vacancies clustering into an agglomerate, and/or of the size distribution of these agglomerates should be done, by means of the method of Positron Annihilation Spectroscopy. This should help to improve the simulations of the strength.

(iii) For the present investigations, the Pd-H and Fe-C systems were chosen not at least because of their role as well-proven model systems. The extension of above described experiments to other alloy systems with a solute element having high trapping potential to deformation induced lattice defects in general, to vacancies in particular, would be very interesting.

(iv) By means of SEM, Krystian et. al found pores of coagulated vacancies in Pd-H [12] which may be interpreted as a strong hint to the process of vacancy agglomeration. Nobody has tried this for Fe-C so far. It is planned to carry out such an experiment on severely deformed Fe0.8wt%C. In addition, not only C can act as defectant in Fe but also Zr. Therefore, investigations on ball milled Fe1at%Zr are planned as well.

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Chapter 9

Abbreviations, Lists

List of Abbreviations

general abbreviations :

$\alpha, \alpha', \alpha + \alpha'$	<i>phases in the Pd – H system</i>
APT	<i>Atom Probe Tomography</i>
bcc	<i>body centered cubic</i>
BM	<i>ball milling</i>
CR	<i>cold rolling</i>
CSD, CDS	<i>coherently scattered domain</i>
DC	<i>direct current</i>
Dis	<i>dislocation(s)</i>
DSC	<i>Differential Scanning Calorimetry</i>
ECCI	<i>Electron Channeling Contrast Imaging</i>
fcc	<i>face centered cubic</i>
GB	<i>grain boundary</i>
HPT	<i>High Pressure Torsion</i>
HV	<i>microhardness with a Vicker's indenter</i>
SB	<i>subgrain boundary and crystallite boundary</i>
SEM	<i>Scanning Electron Microscopy</i>
SPD	<i>Severe Plastic Deformation</i>
TEM	<i>Transmission Electron Microscopy</i>
UTS	<i>ultimate tensile strength</i>
Vac	<i>vacancy/vacancies</i>
XLPA	<i>X – Ray Line Profile Analysis</i>
XRD	<i>X – Ray Diffraction</i>

List of Abbreviations

physical variables :

α	<i>the dislocation configuration parameter</i>
γ	<i>degree of deformation</i>
Γ_A	<i>excess of solute atoms</i>
$d\gamma$	<i>change in surface energy</i>
γ_t	<i>(torsional) shear strain</i>
ϵ_{vM}	<i>von – Mises equivalent strain</i>
κ	<i>a variable marking the ration of pure edge and pure screw dislocations</i>
λ	<i>wavelength</i>
μ	<i>chemical potential</i>
ν	<i>Poisson ratio</i>
Φ	<i>angle of rotation</i>
ρ, ρ_{Dis}	<i>dislocation density</i>
ρ_{loop}	<i>vacancy loop density</i>
σ	<i>standard deviation</i>
σ_M	<i>standard error of the mean</i>
τ	<i>shear stress</i>
Θ	<i>misorientation angle</i>
2θ	<i>scattering angle</i>
Ω, ω	<i>angular velocity</i>
a	<i>lattice constant</i>
$A_{contact}$	<i>contact area in Vickers indentation</i>
b	<i>absolute length of the Burgers vector</i>
b_{loop}	<i>absolute length of the Burgers vector of a vacancy loop</i>
C_{hkl}	<i>dislocation contrast factor</i>
c_{Vac}	<i>vacancy concentration</i>
D	<i>crystallite size</i>
d	<i>grain size</i>
$D(T)$	<i>Diffusion rate</i>
d	<i>thickness (of a sample)</i>
d_1, d_2	<i>length of diagonals in Vickers indent</i>
E_{stor}	<i>stored energy of dislocations</i>
E_{Vac}	<i>stored energy of mono – vacancies</i>
F	<i>(test) load / force</i>
G	<i>shear modulus</i>
ΔH_ν^f	<i>formation enthalpy of a deformation – induced mono – vacancy</i>

List of Abbreviations

I	<i>electric current</i>
$\vec{j}$	<i>current density</i>
l_0	<i>distance between a vacancy loop and a nearby moving dislocation</i>
m	<i>mass</i>
M	<i>molar mass</i>
m	<i>Tabor factor</i>
M_σ	<i>Taylor factor</i>
n	<i>number of solute or solvent atoms</i>
p_{HPT}	<i>pressure used during HPT deformation</i>
r	<i>radius (of a sample)</i>
$r(Pd), r(H), r(Fe), r(C)$	<i>atomic radii</i>
R	<i>radius of a vacancy loop</i>
R_{void}	<i>radius of avoid formed by vacancy agglomerates</i>
RT	<i>room temperature, $RT = 296K$</i>
t	<i>time</i>
T	<i>temperature</i>
T_{deform}	<i>deformation temperature</i>
T_{HPT}	<i>deformation temperature while HPT deformation</i>
T_m, T_m	<i>melting temperature</i>
T_{rec}	<i>recrystallization temperature</i>
V	<i>volume</i>

constants and units :

$at\%$	<i>atomic percent</i>
eV	<i>electron – volt</i>
F	<i>Faraday's constant</i>
GPa	<i>giga pascal</i>
k_B	<i>Boltzmann constant</i>
K_y	<i>material – specific constant</i>
MPa	<i>mega pascal</i>
N_A	<i>Avogadro constant</i>
$wt\%$	<i>weight percent</i>

List of Abbreviations

chemical symbols

<i>Al</i>	<i>Aluminum</i>
<i>C</i>	<i>Carbon</i>
<i>Cu</i>	<i>Copper</i>
<i>Fe</i>	<i>(pure) iron</i>
<i>Fe – C</i>	<i>carbonized iron</i>
<i>H</i>	<i>Hydrogen</i>
<i>Ni</i>	<i>Nickel</i>
<i>Pd</i>	<i>(pure) palladium</i>
<i>Pd – H</i>	<i>hydrogenated palladium</i>
<i>Ta</i>	<i>Tantalum</i>
<i>Ti</i>	<i>Titanium</i>

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