Absolute concentration of free volume-type defects in ultrafine-grained Fe prepared by high-pressure torsion

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A maximum excess volume $\Delta V/V \approx 1.9 \times 10^{-3}$ in ultrafine-grained Fe prepared by high-pressure torsion is determined by measurements of the irreversible length change upon annealing employing a high-resolution differential dilatometer. Since dislocations and equilibrium-type grain boundaries cannot fully account for the observed released excess volume, the present study yields evidence for a high concentration of free volume-type defects inherent to nanophase materials, which is considered to be the main source of their particular properties, such as strongly enhanced diffusivities.
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The amount of excess volume represents a key parameter in the physics of ultrafine-grained and nanocrystalline materials. The excess volume is localized at crystal defects, i.e. lattice vacancies, dislocations and grain boundaries. The amount of excess volume controls the physical properties of materials in a diverse manner. Among the important manifestations of excess volume in solids is the excess energy associated with a defect, such as the grain boundary energy [1,2], or the atomic self-diffusion, which occurs via vacancies, dislocations or grain boundaries [3].

Direct and specific techniques to determine the absolute concentration of excess free volumes are of pivotal importance; however, such techniques are scarce. Information on the concentration of free volumes is usually obtained by indirect ways, e.g. by means of the stored energy or the residual electrical resistance. Only in special cases can volume changes associated with defects be directly deduced by microscopic techniques, e.g. by means of high-resolution transmission electron microscopy in the case of selected grain boundary geometries [4]. Regarding positron annihilation, another specific technique which yields direct information on the local size of free volumes, concentrations of free volumes in practice are often beyond the sensitivity range of this technique [5].

The present letter reports on direct and specific determination of the absolute concentration of excess volume in solids by means of measurements of the time-dependent macroscopic length changes upon annealing employing a high-resolution differential dilatometer. As a case study, the absolute concentration of free volume-type defects is studied on bulk nanophase Fe produced by severe plastic deformation. The study allows an assessment of indirect evidence in recent literature according to which lattice vacancies are introduced in high excess concentration during the processes of structural refinement by severe plastic deformation [6–8]. In the wider scope of current research including bulk metallic glasses and nanoglasses [9], the present study contributes to the fundamental issue of to what maximum concentration free volume-type defects – either localized or non-localized – can be incorporated into a massive metallic solid [9].

Dilatometry is a key experimental technique for determining physical characteristics of solids from which underlying major atomic processes can be elucidated. In a pioneering work, Simmons and Balluffi [10] successfully demonstrated the formation of thermal vacancies in pure metals near the melting temperature by simultaneous measurements of the change in the lat-

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tice constant by X-ray diffraction in combination with the macroscopic length change at thermal equilibrium as a function of temperature (differential dilatometry). Dilatometric techniques were subsequently extended to study vacancy kinetics by measuring the time dependence of the equilibration of thermal vacancies after fast temperature changes in intermetallic compounds [11,12] (time-dependent dilatometry). In the present study the absolute concentration of excess free volumes in ultrafine-grained Fe is determined by measuring the irreversible length change upon annealing. Measurements were performed with a high-precision vertical-difference dilatometer (Linseis, L75VD500 LT). With this set-up, absolute length changes Δl in the order of 30 nm can be measured accurately, which, in combination with specimen lengths l in the 10 mm range, gives direct access to absolute measurements of excess volume concentrations of $3\Delta l/l = \Delta V/V$ down to 1×10^{-5}.

Ultrafine-grained Fe was prepared by the technique of high-pressure torsion (HPT) [13]. Disk-shaped Armco Fe (purity 99.9+%), 30 mm in diameter and 10 mm in height, was torsion-deformed under high pressure (about 5 GPa), giving rise to structural refinement down to a mean crystallite size of 150 nm as determined by scanning electron microscopy. For dilatometry, prism-shaped specimens with a cross-section of 2×2 mm^2 and a height of 7 mm were cut a well-defined distance from the centre of the disk in order to ensure an identical state of deformation in each specimen, corresponding to an equivalent strain of $\varepsilon \approx 30$. The dilatometric measurements were performed in an Ar atmosphere with constant heating rates between 0.75 and 6.0 K min^{-1} simultaneously with measurements of a well annealed and recrystallized defect-free specimen of the same material.

The feasibility of the present approach to unambiguously determine the annealing of non-equilibrium excess free volumes is demonstrated using quenched-in thermal vacancies of well-defined concentration in B2-Fe$_{55}$Al$_{45}$ as a model system. For this purpose, an Fe$_{55}$Al$_{45}$ specimen was initially annealed at 966 K (2 h), to establish thermal vacancy formation, and then water-quenched. The decrease in the vacancy concentration during subsequent equilibration at the lower temperature of 723 K was monitored in situ in the dilatometer via the irreversible shrinkage of the specimen length (Fig. 1). Both the total length change of 3.2×10^{-4} and the time constant of equilibration of 11,400 s agree well with the literature data of thermal vacancy formation [14] and migration [11] of Fe$_{55}$Al$_{45}$, which shows the sensitivity and reliability of the present experimental set-up.

Measurements on ultrafine-grained Fe were performed at constant heating rates instead of isothermally, in order to also take into consideration processes which might occur on a short time scale. Therefore, calibration measurements were run at the applied heating rates in order to check for heating rate-dependent deviations between the temperature of the specimen and that of the integrated temperature sensor. This apparatus-inherent temperature lag was determined by means of the heating rate-independent Curie temperature T_C of the ferro- to paramagnetic phase transition of nickel [15]. The Curie temperature T_C is manifested in a change of the thermal
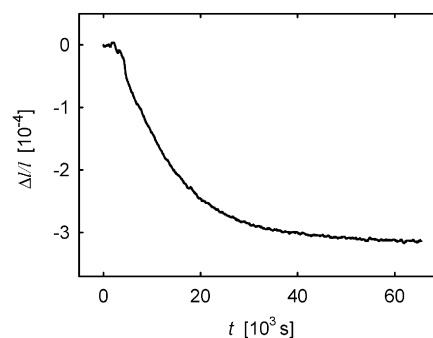

Figure 1. Relative length change $\Delta l/l$ of Fe$_{55}$Al$_{45}$ as function of time due to annealing of remnant vacancies at 723 K after heat treatment at 966 K (2 h) and subsequent water-quenching. Specimen length $l = 20$ mm.

expansion coefficient, giving rise to a λ-shaped curve [16] from which temperature lags of the system between 0.7 and 5.7 K for heating rates between 0.75 and 6.0 K min^{-1} could be determined, respectively. These temperature lags were taken into account for the subsequent measurements on ultrafine-grained Fe. For all dilatometric measurements, the dilatometer was first cooled down to 273 K and then heated up for the measurement with constant heating rates. This ensures that the initial time of a few minutes necessary for stabilizing the heating process is finished so that effects are precisely measurable from slightly above room temperature upwards.

The irreversible annealing of excess free volumes in ultrafine-grained Fe is demonstrated in Figure 2, which shows the length change upon linear thermal cycling of the ultrafine-grained specimen compared to that of the defect-free Fe used as a reference in the differential dilatometry set-up. The difference in the length change which opens up upon initial linear heating (see dotted difference line in Fig. 2) indicates an irreversible shrinkage of the ultrafine-grained sample which is superimposed to the regular linear thermal expansion. In the second linear heating cycle both samples behave the same, which proves the irreversibility of the annealing process during initial heating (Fig. 2).
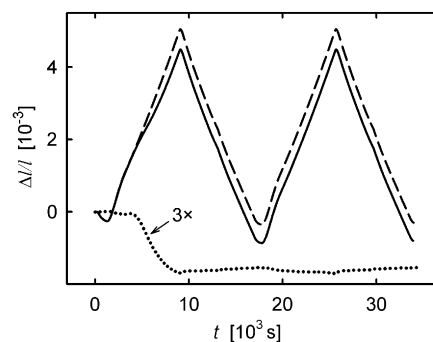

Figure 2. Relative length change $\Delta l/l$ of HPT-deformed Fe (—) and undeformed Fe reference sample (- - -) upon heating and cooling at a constant rate of 3 K min^{-1} (time t). Dotted line: difference (enlarged by a factor of 3) between deformed and undeformed specimen due to annealing of deformation-induced free volume upon first heating cycle.

With increasing heating rate the recovery is shifted to higher temperatures, as is typical of a thermally activated process (Fig. 3). From the temperature shift of the derivative $\partial(\Delta l/l)/\partial T$, which characterizes the maximum rate of length change with respect to temperature, an activation energy of 1 eV can roughly be estimated. For the three different heating rates a similar total irreversible change $\Delta l_{max}/l \approx 6.4 \times 10^{-4}$ occurs, which corresponds to a volume change $\Delta V_{max}/V = 3 \times \Delta l_{max}/l \approx 1.9 \times 10^{-3}$, assuming isotropic distribution and annealing of free volumes.

The observed total volume reduction unambiguously demonstrates the recovery of excess free volumes in ultrafine-grained Fe upon annealing up to a maximum temperature of 756 K. As discussed in the following, free volumes associated with dislocations and equilibrium-type grain boundaries cannot fully account for the total excess free volume. Therefore, the present dilatometric study provides clear evidence for a high concentration of free volume-type defects inherent in the nanocrystalline structure and specific for the strongly athermal preparation route of severe plastic deformation.

Annealing of Fe after high-pressure torsion gives rise to recovery and recrystallization [17]. Scanning electron microscopy after dilatometry reveals a uniform recrystallized structure with an average crystallite diameter d of 410 nm. In the wake of recrystallization, the deformation-induced dislocations are removed. The maximum dislocation density ρ_{disl} introduced by HPT-deformation is of the order of $(2–6) \times 10^{15}$ m^{-2} [18,19]. The removal of dislocations of that density is associated with a relative volume reduction

$$\left(\frac{\Delta V}{V}\right)_{disl} = \gamma_{disl}\rho_{disl} = (0.6 - 1.8) \times 10^{-4} \qquad (1)$$

taking into account the specific excess free volume $\gamma_{disl} = 0.5b^2 = 0.03$ nm^2 of dislocations per unit length in Fe according to elasticity theory [20], where $b = 3^{0.5}a/2$ denotes the value of the Burgers vector with the lattice constant a.

Turning to the decrease in the excess free volume (ΔV_{GB}) associated with the removal of grain boundaries (GB) upon annealing of ultrafine-grained Fe, the relative free volume decrease is given by

$$\left(\frac{\Delta V}{V}\right)_{GB} = 3\delta_{GB}\left(\frac{1}{d_{initial}} - \frac{1}{d_{final}}\right) \qquad (2)$$
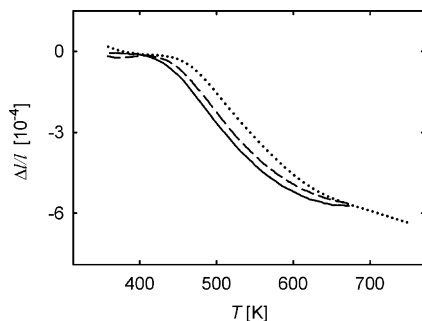

Figure 3. Relative length change $\Delta l/l$ of HPT-deformed Fe as a function of temperature T. Heating rates: 1.5 K min^{-1} (—), 3 K min^{-1} (- - -), 6 K min^{-1} (······). Specimen length $l = 7$ mm.

where $d_{initial}$ and d_{final} denote the initial and final crystallite diameter, respectively. The specific excess free volume of grain boundaries is characterized by δ_{GB}, the volume expansion of the grain boundary per unit area [2]. For nanocrystalline Fe prepared by ball-milling, a value $\delta_{GB} = 0.019$ nm is indirectly deduced from the kinetics of crystallite growth [21]. Direct measurements by high-resolution transmission electron microscopy yield values $\delta_{GB} \approx 0.15a = 0.06$ nm for tilt grain boundaries in Au. Molecular dynamic (MD) simulations of tilt and twist grain boundaries in body-centered cubic metals predict values δ_{GB} ranging up to $0.12a = 0.038$ nm for Mo and $0.25a = 0.072$ nm for Fe [2], which presumably are sensitively dependent on the interatomic potential used for the simulation [22]. With initial and final crystallite diameters of $d_{initial} = 150$ nm and $d_{final} = 410$ nm, a total volume reduction $(\Delta V/V)_{GB}$ of 2.4×10^{-4} or 9.1×10^{-4} is obtained for $\delta_{GB} = 0.019$ or 0.072 nm, respectively (Eq. (2)).

The consideration above shows that, even on the basis of the high δ_{GB}-value of 0.072 nm taken from the MD simulation data, which may be regarded as an upper bound, the total free volumes associated with relaxed grain boundaries $((\Delta V/V)_{GB} = 9.1 \times 10^{-4})$ and dislocations $((\Delta V/V)_{disl} = (0.6–1.8) \times 10^{-4})$ are far from being able to account for the presently observed value of $\Delta V_{max}/V \approx 1.9 \times 10^{-3}$. Therefore, we conclude that at least 40% of this value $\Delta V_{max}/V$ in HPT-deformed Fe is due to additional excess free volume if an isotropic defect distribution and annealing is assumed.

The direct evidence of substantial excess free volumes in nanophase metals obtained from the present dilatometry studies strongly supports recent indirect hints of high free volume concentrations as concluded, for example, from differential scanning calorimetry [6–8] or density measurements [23] and, in particular, from tracer diffusion studies. The excess volume may either be localized inside nanocrystallites as vacancies or vacancy agglomerates, or delocalized at dislocation strain fields or unrelaxed grain boundaries. The latter gives rise to rapid diffusion, much faster than that in conventional grain boundaries, as has been observed in the as-received state prior to structural relaxation in a variety of nanophase metals (for review see Ref. 24), including those prepared by severe plastic deformation [25]. Owing to the direct relation between diffusion and free volumes, excess GB free volume as observed in the present study may be considered as the origin of that enhanced diffusivity. It should be mentioned that the presently observed excess volume, however, may hardly be related to the kind of network porosity recently reported for ultrafine-grained Cu [26] and Cu alloys [27] processed by equal channel angular pressing. The volume fraction of this porosity is below the detection of the present method and this porosity is still present after recrystallization.

In an earlier dilatometric study performed on nanophase titanium [28], excess free volume was attributed to the presence of impurity atoms. However, it should be pointed out that the presently observed high value of the excess volume in ultrafine-grained Fe is similarly also observed by the authors in high-purity Ni ($\Delta V_{max}/V = 3 \times \Delta l_{max}/l = 1.7 \times 10^{-3}$, purity 99.99+%)

[29] prepared by the same technique. This shows that vacancy–impurity complexes may safely be ruled out as a predominant source of the presently observed remnant free volumes, but that these enhanced excess free volumes have to be considered as an inherent characteristic feature of nanophase metals prepared by severe plastic deformation.

The focus of the present letter is on the pivotal issue of the absolute value of the excess free volume; in addition, time-dependent dilatometric studies may also yield information on the kinetics of the structural evolution upon annealing, which is of relevance from a materials science point of view. The activation energy of ca. 1 eV estimated from the shift of the length change with temperature is in good agreement with the activation energy of recrystallization of HPT-deformed Fe obtained from studies of crystallite growth [17]. A closer inspection [29] shows that the broad stage, in which the decrease in length occurs with increasing temperature (Fig. 3), cannot be described by models based on standard Johnson–Mehl–Avrami–Kolmogorov kinetics [30], indicating more complex structural annealing processes of which a detailed analysis is in progress and will be the subject of a forthcoming publication.

In conclusion, with the direct and specific method of high-precision dilatometry, absolute values of the excess free volume, a key parameter for the characterization of physical properties of solids, have been determined in the exemplary case of ultrafine-grained Fe. Evidence for a high concentration of free volumes in addition to that of equilibrium-like grain boundaries and dislocations has been found. For future systematic studies of this kind, a possible orientation dependence of the microstructure on the defect annealing could be taken into account. The present approach extended by detailed kinetic studies might also be fundamental for further studies of volume related basic physical phenomena, i.e. glass transition and plasticity of bulk metallic glasses and nanoglasses.

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