PHILOSOPHICAL MAGAZINE LETTERS, 2017
VOL. 97, NO. 11, 450–458
https://doi.org/10.1080/09500839.2017.1408966

Taylor & Francis
Taylor & Francis Group

Internal stress and defect-related free volume in submicrocrystalline Ni studied by neutron diffraction and difference dilatometry

J. A. Kotzurek[a], M. Hofmann[b], S. Simic[c], P. Pölt[d], A. Hohenwarter[e], R. Pippan[f], W. Sprengel[a] and R. Würschum[a]

[a]Institute of Materials Physics, Graz University of Technology, Graz, Austria; [b]Research Neutron Source Heinz Maier-Leibnitz (FRM II), Technical University of Munich, Garching, Germany; [c]Graz Centre for Electron Microscopy, Graz, Austria; [d]Institute of Electron Microscopy and Nanoanalytics, Graz University of Technology, Graz, Austria; [e]Department of Materials Physics, University of Leoben, Leoben, Austria; [f]Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria

ABSTRACT

A combined study of neutron diffraction and difference dilatometry on submicrocrystalline Ni prepared by high pressure torsion aims at studying the anisotropic behaviour during dilatometry and its relation to internal stress and structural anisotropy. Macroscopic stresses were undetectable in the dilatometer samples. Along with specific tests such as post cold-rolling, this shows that an observed anisotropic length change upon annealing is not caused by internal stress, but can be explained by the inherent microstructure, i.e. the anisotropic annealing of relaxed vacancies at grain boundaries of shape-anisotropic crystallites.

ARTICLE HISTORY
Received 7 August 2017
Accepted 20 November 2017

KEYWORDS
Dilatometry; neutron diffraction; high-pressure torsion; internal strain; vacancy

1. Introduction

The processes of structural refinement by severe plastic deformation, such as high pressure torsion (HPT), as well as the particular mechanical behaviour of these materials are intimately related to their structural defects which are available in highly abundant concentrations [1]. Substantial progress in the understanding of these defects has been achieved over the last years applying a broad spectrum of specific techniques, among which difference dilatometry is a rather powerful one [2]. This technique yielded access to the absolute concentration of deformation-induced lattice vacancies and the grain boundary (GB) expansion as well as to issues of structural relaxation and defect kinetics (see, e.g. [3–5]).

A hitherto not completely clarified issue, however, pertains the pronounced orientation dependence of the irreversible length change which occurs in ultrafine-grained HPT-processed Ni prior to the onset of crystallite growth. A simple model has been recently proposed by the authors which links the anisotropic length change with the annealing of

CONTACT R. Würschum wuerschum@tugraz.at

lattice vacancies at grain boundaries of shape-anisotropic crystallites particularly taking into account the effect of vacancy relaxation [6]. The model could be applied to analyse quantitatively the anisotropic length change occurring in HPT-Ni but, however, has left the question unanswered whether other effects may also cause an anisotropic length change. In particular, macroscopic internal stress may be a primary source of such dilatometric anisotropy. Therefore, in the work presented here, specific dilatometer experiments were designed and performed in order to address the issue of internal stress. Neutron diffraction measurements were applied – to the best of our knowledge for the first time – for directly studying internal stress in this type of HPT-deformed ultrafine-grained metals with a second, independent specific experimental technique.

2. Experimental

In total, four nickel massive discs (99.99+ wt.%, diameter 30 mm, height 10 mm) were deformed by high-pressure torsion for the dilatometry and neutron diffraction studies in the same manner as described earlier (see [3]). From each disc, prism-shaped samples with square bases ($2.5 \times 2.5 \times 7\,mm^3$) were cut out in three different orientations with respect to the HPT-axis, i.e. in axial, tangential and radial direction. Dilatometry was performed with a Linseis L75VD500 vertical, high-precision difference dilatometer (see [3]) under argon flow (5.0) at constant heating rates (between 1.5 and 10.0 $K\,min^{-1}$) from 273 to 773 K. The length change of the ultrafine-grained nickel samples was measured with respect to that of a reference HPT Ni-sample which was pre-annealed to a coarse-grained equilibrium state. The neutron diffraction measurements were performed at the STRESS-SPEC instrument of the FRM II [7]. The 2θ angle was measured for the {311} reflection applying the $\sin^2 \Psi$ method with 17 measurement points in intervals of 10° [8]. Sample orientations relative to the HPT-disc were the same as used for dilatometry. The measuring volume captured by the neutron beam was substantially smaller than the sample size. Evaluation was done with the program StressTextureCalculator (see [9]).

3. Results and discussion

The studies aim to elucidate the anisotropy of the dilatometric length change upon annealing, in particular, whether this anisotropy is caused by internal strain or by structural anisotropy. Figure 1 shows the typical submicrocrystalline structure of high-purity nickel subjected to five turns of HPT deformation. The grains depicted show an elongation along the image plane (axial–tangential plane) in tangential direction as commonly observed for HPT deformation (see [10]).

The said anisotropic dilatometric length change upon annealing is shown in the upper part of Figure 2. Two major regimes can be discerned. In a well-defined relatively narrow stage starting at ca. 470 K, a contraction occurs irrespective of the sample orientation which is due to grain growth in this regime [3]. From the length contraction in this stage, values for the excess volume of the grain boundaries can be deduced [3]. In the preceding temperature regime between 370 and 470 K, a pronounced anisotropy of the length change occurs with a length increase in tangential direction and a length decrease in axial direction. This anisotropic behaviour is highly reproducible as documented in a high number of more than 150 measuring runs on HPT-deformed Ni [11].

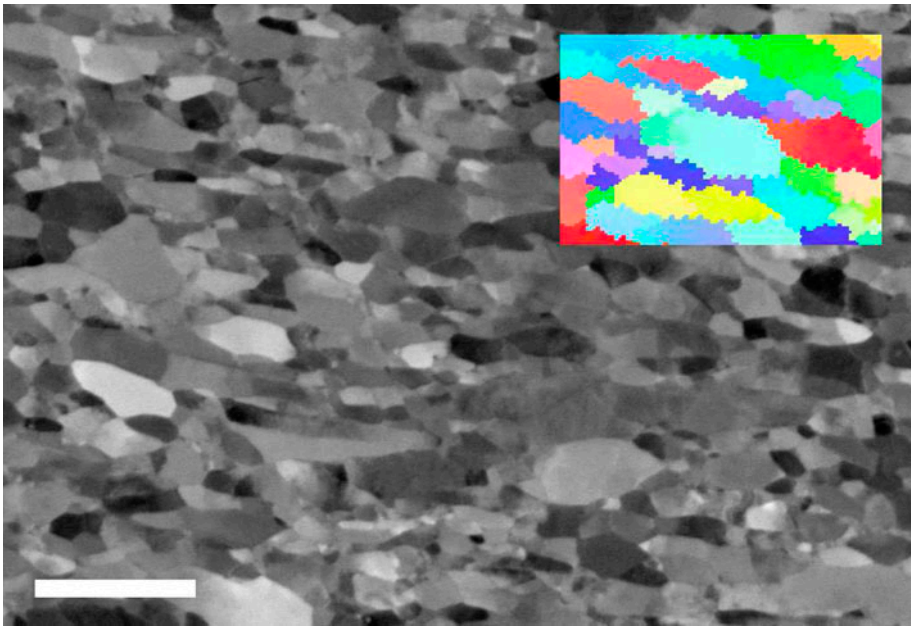

Figure 1. Scanning electron micrograph of an HPT-deformed Ni sample taken at a cross-section in radial direction of the HPT-disc.
Notes: Length of the white bar marks 1 μm. The elongation axis of the crystallites is slightly tilted by an angle of 10° relative to the tangential direction of the disc plan. The insert shows a representative map recorded by the use of electron backscatter diffraction.

The reproducibility with respect to the shape of the $\Delta l/l - T$ curve is much better for tangentially oriented samples that were cut from the outer part of the HPT disc compared to those which were cut from the more central region (compare upper and lower part of Figure 2). Since in all studied parts of the disc, a strain ϵ of at least 12 prevailed during deformation sufficiently high for achieving a homogeneous steady-state microstructure [12], the scatter in the length change data in the inner region presumably is not caused by structural inhomogeneities. This rather indicates that the structural anisotropy is the decisive factor for the length change anisotropy. In fact, the elongation of the crystallites occurs along the shear, i.e. tangential direction and, therefore, the grain elongation is not exactly uniform within a dilatometry sample. For samples cut from larger radii, over the entire sample length the anisotropy axis is reasonably well aligned in the dilatometric measuring direction, i.e. the samples are highly uniform with respect to anisotropy. Whereas for smaller radii, an increasing misalignment of the anisotropy axis with respect to the measuring direction occurs from the middletowards the ends of the rod-shaped dilatometer sample. For all subsequent measurements, tangential samples exclusively from the outer part of the disc were used.

In order to check, whether the anisotropy in length change is caused by anisotropic macroscopic residual stresses induced by the torsional deformation, comparative measurements were performed on HPT-deformed Ni with and without *subsequent cold-rolling*. Such post-deformation has been applied before in different context [13]. The notion is as follows. In principle, macroscopic residual stresses – if present – could cause a length change of the sample during heating since such stress is expected to be relieved upon

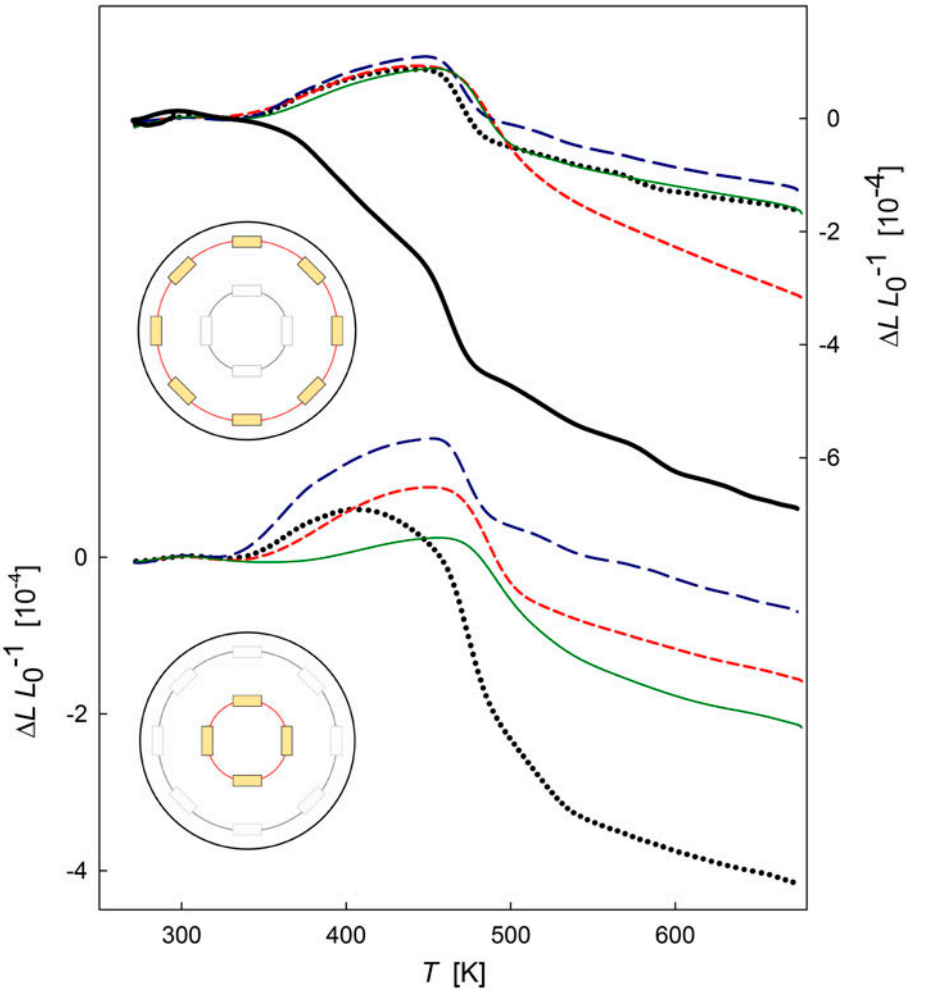

Figure 2. Difference dilatometry of HPT-deformed Ni sample cut out from the HPT-disc with tangential orientation at a radius of 13 mm (strain $\epsilon = 40$; upper set of curves) and of 7 mm ($\epsilon = 20$; lower set of curves) from the disc centre (schematic insets show top-view of the disc).
Notes: $\Delta L/L_0$: relative length change with respect to reference sample. The black—dotted and the blue—dashed curves were measured at a heating rate 3.0 K min^{-1}; the red—short-dashed and the green—thin-solid curves at a rate of 6.0 K min^{-1}. The black—solid curve in the upper part shows the data for a sample with axial orientation for comparison. Note the different scales for the left- and right-handed ordinate axis.

heating due to the decrease of the yield strength giving rise to plastic distortion (see [14]). Any of such HPT-induced residual stresses should, on the other hand, also be relieved by cold rolling the HPT-disc which causes plastic flow (see [15]). Cold rolling itself may cause residual stress, as well. However, this type of stress is of tensile nature in rolling direction (see e.g. [16]) and, therefore, should not give rise to a sample expansion upon annealing-induced stress relief. Cold-rolling was performed from 8 to 4 mm height in steps of 0.5 mm after 16 turns of HPT-deformation at a pressure of 2.2 GPa. Exemplary results of comparative length change measurements with and without cold-rolling are depicted in the upper part of Figure 3. It becomes immediately apparent that subsequent cold rolling

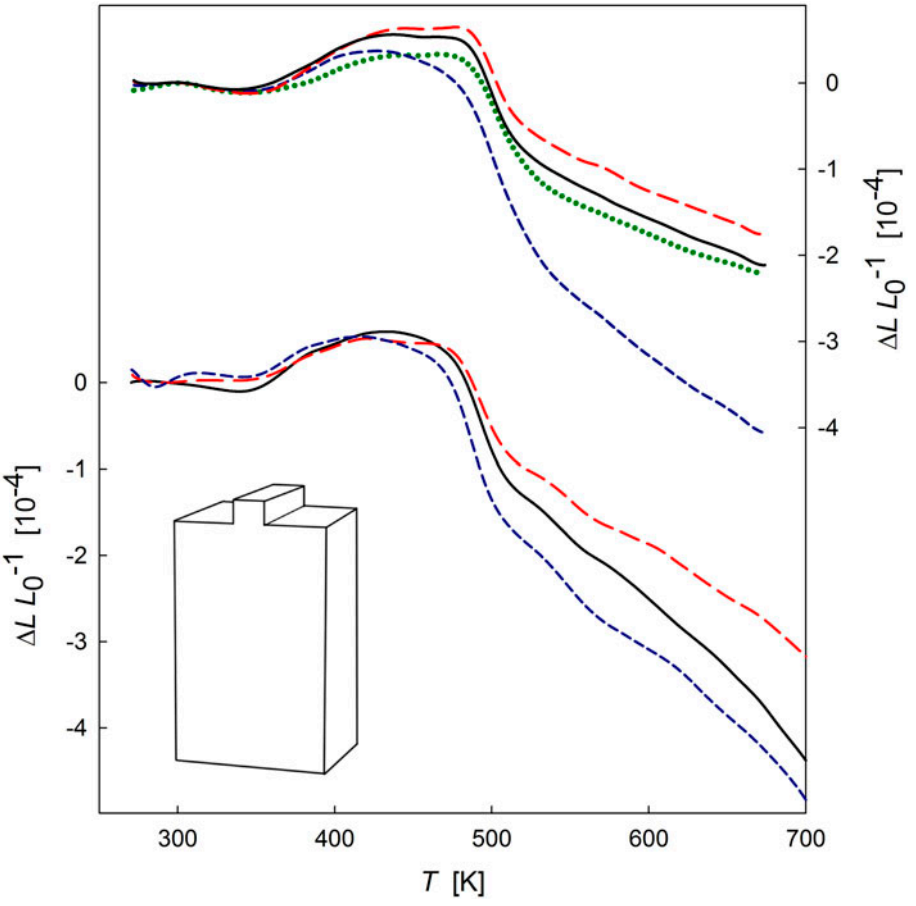

Figure 3. Difference dilatometry of tangentially oriented HPT-deformed Ni samples.
Notes: $\Delta L/L_0$: relative length change measured at heating rate of 3.0 K min^{-1}. Upper set of curves shows effect of cold-rolling after HPT: HPT-deformation up to $\epsilon = 100$ (back—solid curve) and subsequent additional cold-rolling with $\epsilon = 0.5$ (blue—short-dashed); HPT-deformation up to $\epsilon = 70$ (red—dashed) and subsequent additional cold-rolling with $\epsilon = 0.5$ (green—dotted). Lower set of curves shows effect of sample geometry (inset) after HPT with $\epsilon = 40$: Planar abutting face (black—solid); bar-shaped rod end with bar in axial direction (red—dashed) and with bar in radial direction (blue—short-dashed).

does not remove the annealing-induced length increase. This is a strong hint that other causes rather than macroscopic residual stresses are behind this particular length increase.

Since the dilatometric length change is measured by means of a push-rod which rests on the abutting face of the rod-shaped sample, the question arises whether the observed length increase could be caused by a distortion of the sample rather than by a volume expansion. Such a distortion could indicate a stress gradient being relieved during heating. In order to check this item, comparative measurements were performed on sample rods with a bar-shaped end towards the push-rod instead of a plane abutting face (see schematic inset in Figure 3). Tangential samples were prepared with the bar either oriented parallel or perpendicular to the axis of HPT deformation from a disc which was deformed by five HPT-turns at a pressure of 3.4 GPa. The lower part of Figure 3 shows a comparison of three exemplary samples, i.e. two with the different orientations of the bar and the one with the plane end face. For none of the samples a reduced length increase during recovery occurs.

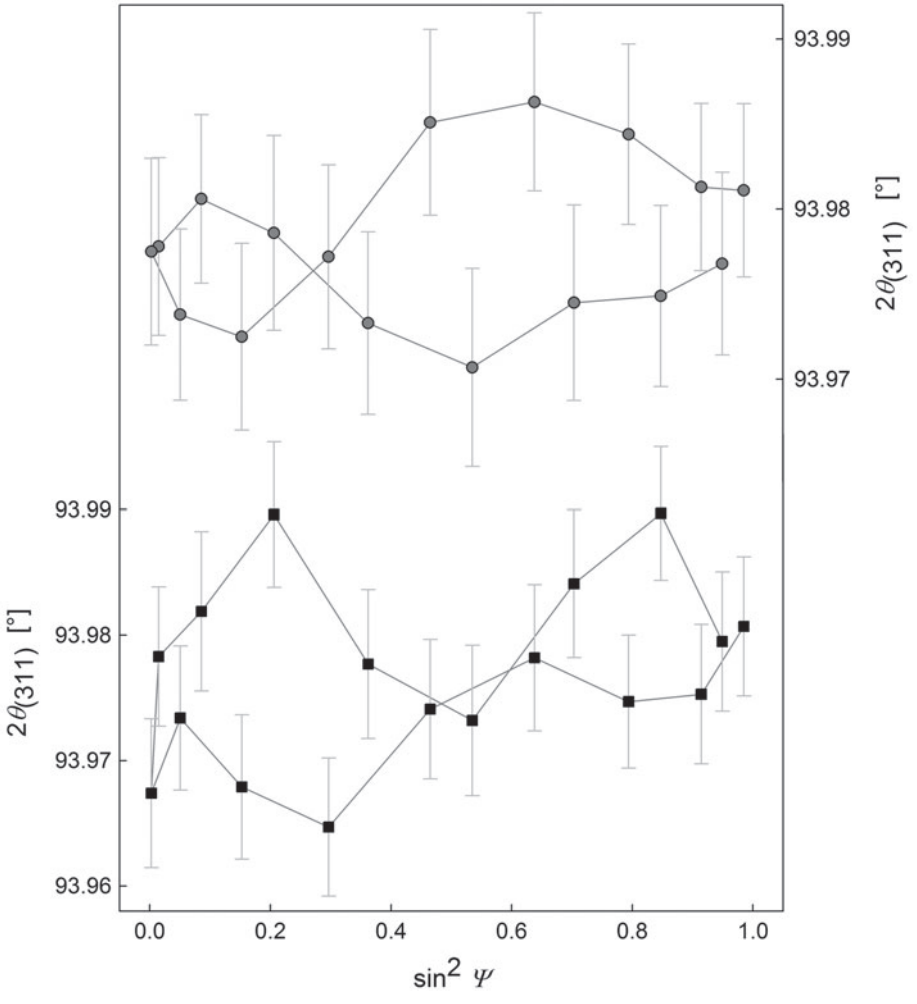

Figure 4. Data of the $\sin^2 \Psi$ neutron diffraction measurement of {311} diffraction peak of dilatometry-shaped samples in axial (grey, circle) and tangential orientation (black, square).

This indicates that the length increase is not an artefact caused by sample distortion, but must be due to volume expansion. In fact, if the length increase would have been caused by a distortion, one of the two samples with bar-shaped end face should exhibit no or at least a lower length increase than the two other samples, which is actually not observed.

In order to get further insight whether the orientation-dependent dilatometric length change is related to release of anisotropic internal stress, measurements of *neutron diffraction* were performed using the same set of different sample orientations and the same sample size as for dilatometry. For each of the three orientations, the diffraction angle was measured for the {311} lattice planes lying parallel to the abutting face of the rod-shaped samples. Figure 4 shows the $\sin^2 \Psi$ plots of an axial and a tangential sample. Neither of these samples, nor the radial sample which is not shown, exhibit a non-zero slope which would be a fingerprint of macroscopic residual stresses [17,18]. The Ψ-splitting indicates at most the presence of some surface stress. It can, however, be safely ruled out that such

surface stresses could give rise to a sample distortion and the anisotropic length change, so much the more because this splitting occurs for both sample orientations. Moreover, for each of the orientations, no significant variation of the (311) peak position can be observed after annealing at temperatures 450 and 500 K within the experimental uncertainties. Since at these temperatures the annealing processes underlying the dilatometric anisotropy have ceased, this further indicates that internal stress may not account for this anisotropy.

In contrast to the small-sized dilatometry samples cut from the HPT-disc, the uncut entire massive HPT disc indeed exhibits residual macroscopic strain as indicated by scans of the {311} diffraction peak along parts of the disc. Most relevant for the present issue is, however, the fact that this macroscopic strains obviously are released upon cutting dilatometry-shaped samples from the HPT disc. Although, such a strain relief to a certain extent can be expected, only the present measurements yield the evidence of complete strain relief.

Summing up the target-oriented systematic comprehensive studies presented above, both dilatometry after post cold-rolling or for samples with different geometries as well as neutron diffraction on the dilatometer-type samples lead to the conclusion that internal strain may be excluded as source for the observed anisotropy of the annealing-induced dilatometric length change (see Figure 2). This rather suggests that the length change anisotropy is related to the pronounced structural anisotropy. Such impact on the annealing behaviour can be expected because an elongated crystallite shape is associated with (i) a higher number of grain boundaries in direction perpendicular to the elongation axis and, hence, with (ii) a reduced diffusion length required for lattice defects to anneal out at GBs. The first issue (i) already manifests in a more pronounced length contraction in axial compared to tangential direction in the narrow stage above 470 K where GBs disappear in the wake of crystallite growth. As analysed in more details earlier [3], the stronger length contraction in axial direction quantitatively scales with the higher number of GBs yielding identical values for the GB excess volume in both measuring directions. This is still the case when the small tilting of the elongation axis with respect to the tangential direction is taken into account [11], what has been neglected in those earlier studies.

The higher number of GBs in axial measuring direction also affects the preceding temperature regime where the length change anisotropy occurs. In fact, prior to the onset of crystallite growth, structural relaxation of HPT-induced GBs occurs as well documented by numerous studies including, e.g. tracer diffusion [19]. If such a relaxation is associated with a decrease of the GB excess volume, the corresponding length contraction in axial measuring direction would be higher than in tangential direction due to the higher number of relaxing GBs in axial direction. However, this could at most account for a reduced contraction in tangential direction, but not for the observed expansion.

We therefore have to conclude that it is the reduced diffusion length required for lattice defects to anneal out at GBs perpendicular to the elongation axis which causes the dilatometric anisotropy. Lattice vacancies occur in high abundant concentrations of several 10^{-4} in HPT-Ni and become mobile [20] in the temperature regime where the anisotropic length change occurs. Since vacancies predominantly anneal out perpendicular to the axis of crystallite elongation owing to the reduced diffusion length to reach the GB sink, shrinkage occurs in this direction which is indeed the case for the axial measuring direction (see Figure 2). Consequently, at first sight, along the axis of crystallite elongation no length change at all, rather than an expansion, would be expected for the limiting case of

strong elongation when no vacancy annealing occurs in this direction. Recently we could propose, however, a simple model according to which such an expansion upon orientation-dependent vacancy annealing is a mere consequence of vacancy relaxation [6]. In fact, when relaxed vacancies are replaced by atoms, the lattice expands in all spatial directions which gives rise to a dilatometric expansion in the tangential direction where no vacancy annealing occurs. Assuming entirely anisotropic vacancy annealing due to the elongated crystallite shape, the proposed model of vacancy relaxation allows to determine both the vacancy volume and concentration from the ratio or difference of the length contraction in axial direction and the length expansion in tangential direction, respectively. In this way, a vacancy volume between 0.60 and 0.64 of the atomic value was obtained in reasonable agreement with theoretical predictions [6].

In summary, we could show that the anisotropy in dilatometric length change upon annealing is not caused by macroscopic internal stress, but rather by the anisotropic annealing of relaxed vacancies at GBs of shape-anisotropic crystallites. Neutron diffraction revealed that internal stress obviously is being relieved upon cutting the dilatometer samples from the disc. The access to anisotropic processes turns out as an important advantage of dilatometry compared to other techniques of thermal analysis, as for instance calorimetry.

Acknowledgements

This work is based upon experiments performed at the STRESS-SPEC instrument operated by the Helmholtz Zentrum Geesthacht (HZG) at the Heinz Maier-Leibnitz Zentrum (MLZ), Garching, Germany. Financial support provided by HZG to perform the neutron scattering measurements is acknowledged.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This work is financially supported by the Austrian Science Fund (FWF) [grant number P25628-N20].

ORCID

J. A. Kotzurek http://orcid.org/0000-0002-6929-1497
P. Pölt http://orcid.org/0000-0001-6910-5095
A. Hohenwarter http://orcid.org/0000-0001-9827-9828
R. Pippan http://orcid.org/0000-0003-4723-3170
W. Sprengel http://orcid.org/0000-0002-8335-8555
R. Würschum http://orcid.org/0000-0003-4624-4433

References

[1] D. Setman, E. Schafler, E. Korznikova and M.J. Zehetbauer, Mater. Sci. Eng. A 493 (2008) p.116.
[2] W. Sprengel, B. Oberdorfer, E.M. Steyskal and R. Würschum, J. Mater. Sci. 47 (2012) p.7921.

[3] E.-M. Steyskal, B. Oberdorfer, W. Sprengel, M.J. Zehetbauer, R. Pippan and R. Würschum, Phys. Rev. Lett. 108 (2012) p.055504-1.
[4] B. Oberdorfer, D. Setman, E.-M. Steyskal, A. Hohenwarter, W. Sprengel, M. Zehetbauer, R. Pippan and R. Würschum, Acta Mater. 68 (2014) p.189.
[5] J.A. Kotzurek, W. Sprengel, M. Krystian, S. Simič, P. Pölt, A. Hohenwarter, R. Pippan and R. Würschum, Int. J. Mater. Res. 108 (2017) p.81.
[6] J.A. Kotzurek, E.-M. Steyskal, B. Oberdorfer, A. Hohenwarter, R. Pippan, W. Sprengel and R. Würschum, Appl. Phys. Lett. 109 (2016) p.021906-1.
[7] M. Hofmann, W.M. Gan and J. Rebelo-Kornmeier, J. Large Scale Res. Facil. 1 (2015) p.1.
[8] M. Zehetbauer, E. Schafler and T. Ungár, Int. J. Mater. Res. 98 (2007) p.290.
[9] C. Randau, U. Garbe and H.-G. Brokmeier, J. Appl. Crystallogr. 44 (2011) p.641.
[10] G.B. Rathmayr, A. Hohenwarter and R. Pippan, Mater. Sci. Eng. A 560 (2013) p.224.
[11] J. Kotzurek, *Structural Anisotropy and Lattice Defects in Submicrocrystalline Metals Studied by Difference Dilatometry and Neutron Scattering*, Doctoral thesis, Graz University of Technology, Austria, 2017.
[12] R. Pippan, F. Wetscher, M. Hafok, A. Vorhauer and I. Sabirov, Adv. Eng. Mater. 8 (2006) p.1046.
[13] D.A. Price, S.W. Williams, A. Wescott, C.J.C. Harrison, A. Rezai, A. Steuwer, M. Peel, P. Staron and M. Koçak, Sci. Technol. Weld. Joining 12 (2007) p.620.
[14] B. Chen, A. Skouras, Y.Q. Wang, J.F. Kelleher, S.Y. Zhang, D.J. Smith, P.E.J. Flewitt and M.J. Pavier, Mater. Sci. Eng. A 590 (2014) p.374.
[15] S. Kalpakjian and S. Schmid, *Manufacturing Processes for Engineering Materials*, Pearson Education, Upper Saddle River, NJ, 2008.
[16] M. De Giorgi, Int. J. Fatigue 33 (2011) p.507.
[17] B. Eigenmann and E. Macherauch, Materialwiss. Werkstofftech. 26 (1995) p.148.
[18] B. Eigenmann and E. Macherauch, Materialwiss. Werkstofftech. 26 (1995) p.199.
[19] S.V. Divinski, G. Reglitz, H. Rösner, Y. Estrin and G. Wilde, Acta Mater. 59 (2011) p.1974.
[20] W. Wycisk and M. Feller-Kniepmeier, J. Nucl. Mater. 69–70 (1978) p.616.