Persistence of ultrafast atomic diffusion paths in recrystallizing ultrafine grained Ni

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Tracer self-diffusion is investigated in ultrafine grained Ni prepared by high pressure torsion. Under identical diffusion annealing conditions the ultrafine grained structure of less pure Ni remains stable, while recrystallization and subsequent grain growth occur in high purity Ni. Nevertheless, qualitatively similar ultrafast diffusion rates are measured in the samples of both purity levels. A model explaining retention of deformation-induced ultrafast diffusion paths in recrystallized Ni in terms of solute redistribution in front of the moving boundary is suggested.
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Extensive investigations of ultra-fine grained (UFG) materials obtained by severe plastic deformation (SPD) during the last decades revealed many attractive kinetic properties of these materials related to ultrafast diffusion rates in the as-processed state [1–3], which were measured in, e.g., UFG Cu [4] and Ni [1,5]. Simultaneously, it was found that SPD processing is often accompanied by the formation of a pronounced hierarchy of kinetic properties of the internal interfaces [6]. A typical diffusion profile in as-processed UFG material exhibits a "slow" branch at shallow penetration depths (associated with general high-angle grain boundaries which are identical to the boundaries in well-annealed coarse-grained polycrystals), and a deeper branch corresponding to "high-diffusivity" ("fast") paths. An extensive discussion of such paths in terms of existing levels of diffusion hierarchy in SPD materials is given in Ref. [7].

In our previous paper [8], the existence of ultrafast diffusion paths was established in UFG Ni of 99.99 wt.% (4N) and 99.6 wt.% (2N6) purity levels produced via high-pressure torsion (HPT). In 4N Ni, these specific short-circuit paths for atomic transport resulted in the low-slope penetration profiles at large depths, co-existing with a steeper, convex branch at shallow depths. The latter turned out to be a 'finger-print' of recrystallization of the UFG microstructure of pure Ni during diffusion annealing, and it was a subject of our previous study [8]. While the ultrafast diffusion paths in 2N6 Ni after HPT processing are qualitatively similar to their counterparts in UFG Ni produced by equal channel angular pressing [5], the existence of these ultrafast paths in 4N Ni was very surprising in view of the complete recrystallization of this material during corresponding diffusion annealing treatments. How do the ultrafast diffusion paths survive the recrystallization and grain growth? What is the nature and mechanism of the unusual stability of these paths? These are the main subjects of the present paper.

Nickel samples of nominally 4N and 2N6 purity levels were cut in the form of 1 mm thick discs of 10 mm in diameter by spark erosion and ground. The discs were subjected to HPT treatment at room temperature under a pressure of 2 GPa and applying 5 rotations.

The microstructure was characterized with a FEI Nova NanoSEM 230 scanning electron microscope (SEM) equipped with electron back scatter diffraction (EBSD) attachment, which was operated at 18 kV. The average grain sizes of about 100 and 200 nm in 2N6 and 4N Ni, respectively, were determined.

The Ni self-diffusion was studied employing the ^{63}Ni radiotracer. The radiotracer solution was dropped on the polished sample surface and dried. The samples were wrapped in Ni foil, sealed in a silica tube and subjected to the given diffusion annealing treatments. The diffusion penetration profiles were determined by the serial-sectioning technique using a precision parallel grinder. The section thickness was determined from the density and the mass reduction by weighing the samples on a microbalance. The section radioactivity was measured by a Liquid scintillation

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analyzer (TRI-CARB 2910 TR PACKARD, Canberra Co). Further experimental details are given in Ref. [8].

The penetration profiles of self-diffusion in HPT-processed Ni are shown in Figure 1a and b for 2N6 and 4N purity materials, respectively. They are plotted in coordinates of the relative specific activity *vs.* the penetration depth squared, since the measurements are performed in the C type regime after Harrison's classification [9]. In two experiments the samples were pre-annealed, Figure 1b, in order to induce recrystallization before the actual diffusion annealing (for details see Ref. [8]).

The striking feature of the penetration profiles measured for GB self-diffusion in UFG Ni of 4N purity is that they reveal systematically two distinct branches, a near-surface one at shallow depths below 4–6 μm; and a significantly deeper one, Figure 1b. It is important that the former branch is nearly absent in the case of less pure 2N6 Ni (where it is almost exclusively caused by grinding-in effects), Figure 1a, and that it reveals a remarkable kink in the case of 4N Ni, see Ref. [8]. However, the present work is focused on the deep branches of the penetration profiles, which are related to the ultrafast atomic transport and are observed in both materials.

The effective diffusivities, D^{eff}, corresponding to the deep branches of the concentration profiles were determined assuming constant-source initial conditions, and they are presented in Figure 2 as a function of annealing time.

It was checked that the open porosity, as it was found in UFG Cu [10], is absent in the present case of HPT Ni. Thus, the internal interfaces, which are probably in a specific, deformation-modified (often referred to as "non-equilibrium" [11]) state introduced by SPD, may exhibit accelerated GB diffusion [7].

The relaxation time, τ, of the "non-equilibrium" GB state can be estimated employing the disclination-based concept [11]:

$$\tau = \frac{d^3 kT}{A \delta D_{\mathrm{gb}} G \Omega_a}. \tag{1}$$

Here d is the grain size; G is the shear modulus; Ω_a is the atomic volume of Ni; A is a geometrical factor of the model; δ is the GB width; and kT has its usual meaning. The key problem of this expression is represented by the GB diffusion coefficient, D_{gb}, which has to be employed in estimates. It is the diffusion coefficient of *relaxed* high-angle GBs, as they are present in well-annealed high purity polycrystalline Ni,
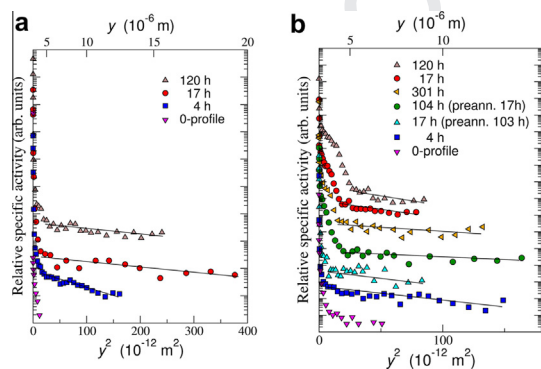

Figure 1. Penetration profiles measured in 2N6 (a) and 4N (b) Ni materials at 423 K for different diffusion times (indicated). The solid lines represent the fits according to the complimentary error function solution for GB diffusion. The zero-profiles represent the resulting tracer distribution without diffusion annealing, see Ref. [8].
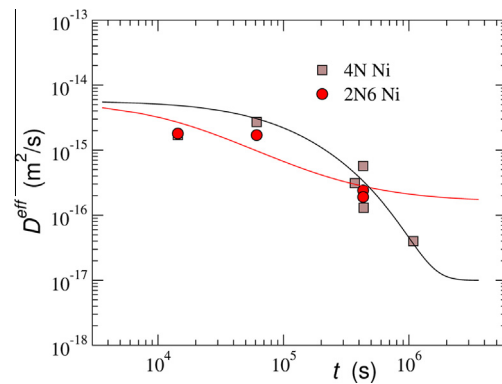

Figure 2. Diffusion coefficients as a function of time (anneals at 423 K). The curves are drawn only as a guide for the eye and correspond to the present understanding of a two-stage relaxation of the deformation-modified state of high-angle GBs in HPT Ni, see text.

which has to be used in Eq. (1) [5]. This can be understood in terms of an inhomogeneous distribution of excess free volume in deformation-modified GBs with areas of "good" and "bad" match [12]. Using further the value of $A = 200$ [5], the relaxation times are estimated to be equal to 7 and 56 h in 2N6 and 4N Ni, respectively. This relatively large difference between the two materials stems from the strong dependence of τ on the grain size, Eq. (1).

These estimates are in a general agreement with the present experimental diffusion data – the diffusion coefficients are nearly equal for 4 and 17 h annealing treatments, and decrease by an order of magnitude after diffusion annealing for more than 120 h, Figure 2. This decrease may be explained by the relaxation of the deformation-modified interfaces in HPT Ni. However, in line with our previous observation in UFG Ni [5,12], these values do not approach those for relaxed high-angle GBs (which would be about 10^{-21} m²/s or even less, depending on the segregation level of residual impurities). The existence of metastable non-equilibrium GB states was predicted in atomistic computer simulations of Rittner and Seidman [13]. In the 3N-dimensional configuration space of GB structures (here N is the number of atoms per unit area of the GB) the metastable and equilibrium states are separated by the states of higher energy. Thus, while the kinetics of relaxation of the initial GB state toward the metastable one is given by Eq. (1), the relaxation to the equilibrium state requires nucleation. We propose that because of the relatively low homologous temperature of the diffusion experiment (about $0.24 T_{\mathrm{m}}$, where T_{m} is the melting point of Ni) the nucleation rate of truly relaxed GB "phase" may be negligibly small and the GBs can preserve their metastable configuration for a long time (this is also consistent with the model of Ref. [12]).

The kinetics of recrystallization of 4N Ni during isothermal annealing at 423 K was investigated in detail in our previous study [8]. The Johnson–Mehl–Avrami–Kolmogorov (JMAK) formalism was applied to describe the kinetics of heat release during isothermal annealing at 423 K, and no signal was recorded after about 1 week (recrystallization is presumably finished). However, ultrafast diffusion paths withstand this annealing, Figure 2.

In Figure 3, microstructure of UFG 4N Ni after 130 h of annealing at 423 K is presented. A homogeneous coarse-grained microstructure is observed with a small amount of islands of residual ultrafine unrecrystallized grains. The average volume fraction of the unrecrystallized fraction, count-