From an understanding of structural restoration mechanisms towards a selective processing of extreme nanolamellar structures

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Abstract. It has been successfully proven that severe cold deformation can be used to generate bulk nanostructured materials. However, there is a limit to grain refinement, as recovery processes, together with grain boundary and triple junction motion, occur to continuously fragment and remove grains. Although believed to be mechanically driven at low temperatures, it is clear that such movement can be thermally assisted, as reflected in decreased grain aspect ratios at elevated deformation temperatures. Interestingly, for tantalum, a different behaviour can be found. Grain aspect ratios after high pressure torsion increase steadily up to deformation temperatures of 673 K before dropping again. Moreover, extremely large aspect ratios of 10 can be generated. The reasons for this behaviour are discussed and it is suggested from results based on nickel that this phenomenon can be adapted to any metal. This offers the possibility to selectively process materials with extreme grain aspect ratios, to achieve structures which are thought to be the key to the design of materials that combine both, exceptional strength and good damage tolerance.

1. Introduction
Severe cold working of metals significantly enhances their strength as their grain size is decreased efficiently, but along with the increase in strength, generally ductility and fracture toughness are reduced [1–3]. Overcoming this strength-ductility trade-off remains challenging as further strain hardening in such materials is hard to realize. Nevertheless, results for nanostructured materials showing high strength in combination with good ductility have occasionally been reported. These studies rely on the introduction of nanotwins inside grains, or the use of proper annealing treatments to produce bimodal grain size distributions, which were shown to be useful strategies to maintain ductility, despite the observed strength increase [4–7]. Although these results seem promising, especially the concept of nanotwins is not easily transferable to any bulk material system, as synthesis is mainly limited to deposition processes [4,5] or dynamic plastic deformation at cryogenic temperatures [8]. Moreover, generation of suitable bimodal grain size distributions with sufficient volume fractions of coarser grains by annealing procedures is also not easy to achieve. In many cases nanocrystalline (NC) materials remain stable up to certain temperatures, but then coarsen rapidly, often accompanied by abnormal grain growth, while in some cases even though a bimodal grain structure was produced, ductility was not enhanced compared to the as-processed state [9–11].
Results obtained on bulk nanostructured materials, synthesized by high pressure torsion (HPT) suggest, however, that the elongated grain shape, arising from the deformation process, can be effectively used to process materials combining enhanced strength and acceptable toughness values [12]. Similar results were obtained for cold rolled tungsten foils in which elongated grain structures were also developed [13], suggesting that this approach could be applicable work for any kind of material.

These excellent combinations of strength and toughness result from highly anisotropic properties that can be measured in such nanolamellar structures. The pronounced toughness anisotropy arises due to the preferred crack path in sub-micron or nanocrystalline (NC) materials, which in most cases is along the numerous grain boundaries [12]. This leads to low energy consuming crack paths when pre-cracks are introduced parallel to the elongated grain structure, while testing in either of the two directions perpendicular to this results in considerably higher toughness values, as intergranular fracture occurs, leading to crack deflection and delamination, both of which contribute to the measured toughness values [12]. This suggests that one of the essential structural parameters to overcome the strength-toughness conflict in high strength materials is the aspect ratio. Cold working of metals therefore might be an easy and effective approach to produce such highly elongated grain structures. Unfortunately, for most pure single phase materials or alloys, although deformed to severe strains at low homologous temperatures, typically aspect ratios only of 2 – 4 can be obtained [14]. The main restriction for grain elongation and refinement is the occurrence of dynamic recovery mechanisms. These processes, including deformation induced grain boundary (GB) migration [15] and motion of triple junctions (TJs) [16], continuously shorten and fragment grains. Although it is generally recognized that the aspect ratio decreases with an increase in deformation temperature [14, 17–19], recent experiments on tantalum have shown that up to a certain deformation temperature, the aspect ratio can even increase [20]. It can be expected that despite the temperature increase, recovery processes are still occurring albeit inefficiently, as otherwise the grains would become more globular.

The present work will summarize the main findings about GB and TJ motion in highly strained structures with a special emphasis on recent results obtained on tantalum. Additional experiments on nickel suggest that the trend of increasing aspect ratios up to specific deformation temperatures is a general one and allows further conclusions how such nanolamellar structures can be generated.

2. Recovery after large and severe strains

Large and severe strains cause significant grain refinement in metal structures as dislocations are continuously produced, stored and rearranged, which subdivides the coarse grains. Details of this grain fragmentation process can be found elsewhere [17, 21]. The most important results are that with increasing strain the structural size decreases while the misorientation is increasing, but refinement terminates after a certain strain, when an equilibrium between refinement and recovery is obtained. On the structural scale, this necessitates that grain boundaries have to be removed. Such net removal of grain boundaries already starts at moderate strain levels of ε > 1 [22], with the underlying processes being GB and TJ motion [15, 16].

For TJ migration the main driving force stems from the dihedral angles, θ, being far from their equilibrium value, i.e. 120° for a junction consisting of three equal high angle grain boundaries (HAGB) [23]. TJ motion tries to shift θ towards the equilibrium value, thereby lamellae can disappear or reduce their aspect ratio [23, 24], as illustrated schematically in figure 1. After severe deformation, the dihedral angles will be far from equilibrium and enlarged driving forces for TJ motion can be expected during annealing. Additionally, during deformation of such structures the thickness of the lamellae will reduce further, which could decrease θ and thereby cause an increased tendency for TJ migration. However, one should be careful to conclude that generally thin lamellae will have smaller dihedral angles, thus higher driving forces for TJ migration. Although, measurements on severely rolled aluminum point in this direction [24], the observed scatter is relatively large and local grain boundary diffusion could also cause an increase of θ [25].
On the other hand, GB migration during deformation can fragment adjacent grains, which may shrink further either by GB migration or subsequent movement of the newly created TJs, see figure 1. Because this kind of GB migration can be observed even at low deformation temperatures it is generally accepted that it is mechanically activated. Nevertheless, the driving forces are still controversially debated. Coupling of GBs with shear stresses was suggested to cause migration of the GBs [26–28], while other studies have provided clear evidence for the role of plastic strain [29]. The latter would be in line with the formation of deformation textures after severe deformation similar to the ones expected for dislocation based plasticity [30]. Moreover, calculations have shown that strain energy differences between grains yield reasonable values for the driving force of several MPa [30]. However, on the atomic scale grain boundary migration has been attributed to the movement of disconnections i.e. GB steps associated with a dislocation [31]. Such GB defects can be formed easily due to the interaction of lattice dislocations with GBs [31,32]. Especially in cases when the mobility of disconnections is limited they presumably pile up, leading to the formation of macro steps [28,31]. The bulging of GBs that leads to fragmentation of neighboring grains, see figure 1, may therefore be directly associated to the formation of such macro steps.

![Figure 1. Schematics showing structural restoration mechanisms occurring during large or severe strains; a) movement of triple junctions, and b) movement of grain boundaries. Both processes can fragment or shrink individual lamellae, leading to a structural coarsening and thus limiting refinement and the aspect ratio.](image)

Because both GB and TJ migration counteract grain elongation, the generation of bulk nanostructured materials with enhanced aspect ratios necessitates the development of strategies that subdue them to a great extent. Furthermore, deformation modes or temperatures where shear band formation may occur should also be avoided, as such localized shear can fragment lamellae as well [16,33]. Strain path changes have been suggested as a means to overcome the problem of structural recovery and to suppress these processes, leading to a reinvigoration of boundary generation, offering the possibility for further grain refinement [33]. However, results on structures already deformed to saturation have shown that a strain path change does not necessarily result in further refinement. On the contrary, pure ultrafine-grained copper synthesized by HPT and further deformed by cold rolling revealed, up to strains of ε ~ 1, even a slight coarsening of the grains [15] (see figure 2). At higher rolling strains, the lamellae were refined again, although no significant reduction of the minimum lamella spacing compared to the as-HPT deformed state could be achieved.

As indicated, GB and TJ migration are thought to be mainly mechanically induced, especially when severe deformation is carried out at low homologous temperatures. Nevertheless, it can be expected that they are thermally facilitated, which explains the observation of larger grains with reduced aspect ratios after severe deformation at elevated temperatures [14,17–19].

Accordingly, one would intuitively think that very large aspect ratios could be generated during cryogenic deformation, where the restoration processes can be retarded more efficiently. However, recent results on tantalum have shown a different trend, where the aspect ratio increased with deformation temperature up to 673 K [20], see figure 3. The reason for this distinct increase in grain elongation is related to a much stronger length increase of the long grain axis compared to the minor axis, as shown in figure 3. As the minimum grain dimensions continuously increase with deformation temperature it is clear that the overall restoration processes have to increase. Nevertheless up to 673 K recovery is still clearly insufficient to fragment the lamellae, as the length of the major grain axis increases in this temperature range.
Figure 2. Structural evolution of ultrafine grained Cu processed by HPT and subjected to further cold rolling. Instead of a further refinement of the lamellae, structural coarsening proceeds up to strains of $\varepsilon \sim 1$.

Figure 3. Evolution of the major and minor grain axes, as well as the aspect ratio, of tantalum severely deformed by HPT at different temperatures. Data taken from Ref. [20].

It is not surprising that the structures deformed at 77 K and RT do not differ significantly, as experiments have already shown, that the grain size changes at low homologous temperatures are not pronounced any more, as thermal activation is negligible and mechanically induced motion prevails [14,30]. In fact, as the structures generated after severe deformation at low temperatures consist of rather planar GBs, thermally driven GB migration will not play a role until the structure changes into a curved, more globular one, for instance by thermally induced TJ motion. Such structural changes have already been observed due to thermally induced TJ motion during static annealing of severely deformed structures [34]. However, thermally induced TJ motion will occur only above a certain temperature, accessible from static annealing treatments. For tantalum this temperature was found to lie between 673 K and 773 K, exactly the temperature regime were the aspect ratio starts to drop again [20], (figure 3). The occurrence of a critical temperature $T_0$, above which frequent TJ motion takes place seems to be related to the presence of lattice defects at temperatures below this, as loose dislocations and interconnecting boundaries within the lamellae act as pinning points for TJ motion [35]. Therefore, fast TJ motion is unlikely to occur during deformation at lower temperatures as the probability of intragranular defect storage, and so the number of pinning points, are enhanced.
Consequently, the continuous increase of the aspect ratio with HPT temperature below $T_0$ has to be explained by a reduction of grain fragmentation events when the deformation temperature is increased. For tantalum the GBs appeared more flat at elevated processing temperatures, and bulges, as marked by arrows in figure 1, can be rarely observed, although the mobility of the GBs had to increase as larger lamellae thicknesses can be observed for higher deformation temperatures. The explanation for these results might be directly linked to the mobility of disconnections. TEM studies have revealed that on the mesoscale grain boundary migration is caused by the movement of disconnections. These boundary defects can be created at any temperature by the interaction of lattice dislocations with GBs, however, their mobility, will differ markedly [31]. At low temperatures, and hence limited mobility, they will pile up frequently, causing the formation of macro steps [31], which appear similar in size to the bulges that can be observed during deformation [15,20] and in turn lead to fragmentation of adjacent grains. During processing at elevated temperatures, when their mobility is increased, macro step formation will occur less frequently but the GB migration rate will be larger. This would explain not only why the minor axis of the tantalum grains slightly increased with temperature but also why fragmentation occurred rarely, enabling the generation of large grain elongations.

For this reason the main conclusion in [20] was that the resulting grain aspect ratio after severe deformation reaches a maximum at a temperature low enough to maintain enough lattice defects for effective TJ pinning but high enough to prevent frequent grain fragmentation events caused by GB migration. Of course, this will only hold true, for homogenous deformation, where the generated structure results from a balance between refinement and the restoration processes and will not be fulfilled for deformation modes, alloys or temperatures where intense shear banding is present. Such localized shear can again lead to fragmentation of the lamellae and thus deviation from the above description [16,33].

3. Generation of extreme nanolamellar structures – a possibility for all metals?
These conclusions on the occurrence of large aspect ratios in tantalum suggest that the generation of such structures should not solely be restricted to high melting point metals like tantalum. Although its high melting point certainly eases such observations, the principle should work for fcc metals or lower melting point metals as well. For this reason, we carried out a similar study on pure nickel with 99.99% purity. Disks with 8 mm diameter and a thickness of 0.8 mm were deformed by quasi-constrained HPT at different deformation temperatures, ranging from 77 K to 673 K. One sample deformed at 298 K was used for static annealing treatments to identify the onset of structural coarsening. The microstructures were analyzed in the radial direction at a radius of $r = 3$ mm using electron backscatter diffraction (EBSD), see inset image in figure 4. For quantification of the structural sizes a standard software package was used. Additional microhardness measurements were taken on the statically annealed samples.

Annealing treatment on the samples HPT deformed at 298 K showed typical recovery up to temperatures of about 423 K, see figure 4. As the grain size remained stable within this temperature range, the decrease in hardness occurs due to dislocation annihilation. Between 423 K and 473 K recrystallization and grain growth occurs, resulting in grain sizes up to 5 $\mu$m in size. Moreover, grains with still smaller size appear already equiaxed.

Figure 5 shows inverse pole figure (IPF) maps of the structures deformed at different deformation temperatures. Although the differences are as pronounced as for tantalum, similar trends can be observed. The grains become more elongated with increase of the HPT deformation temperature, with a maximum aspect ratio observed for deformation at 418 K. For higher HPT deformation temperatures, the aspect ratio dropped again, see figure 5.
Figure 4. Room temperature microhardness of a nickel sample HPT-deformed at 298 K as a function of the annealing temperature. Microstructures remain stable up to ~ 423 K, as only defect recovery occurs. For temperatures above this fast coarsening of the structure takes place.

Figure 5. Representative inverse pole figure maps of nickel structures (radial view) deformed at different temperatures. At temperatures up to 418 K the grain aspect ratio clearly increases.

Similar to the observations for tantalum samples, the onset of structural coarsening during static annealing and the deformation temperature where the aspect ratio starts to reduce are again similar. Although grain elongations are not as pronounced as for tantalum, the results on nickel show that elevated deformation temperatures may be the key to obtaining structures with pronounced aspect ratios.

4. Conclusions and Outlook
Experiments on pure tantalum and nickel have shown that processing at elevated temperatures leads to the formation of ultrafine-grained structures with pronounced grain aspect ratios. A maximum of the aspect ratio can be obtained by deformation at temperatures, \( T_0 \), similar to that leading to first structural coarsening during static annealing. Despite that the recovery mechanisms increase with temperature, these mechanisms may be insufficient to promote fragmentation, thereby enabling the observed increase in grain elongation. The reason for this seems to arise from inefficient movement of triple junctions at temperatures below \( T_0 \) due to pinning by intragranular defects or at dislocation boundaries. Moreover, fragmentation events of adjacent grains due to grain boundary migration occur less frequently at elevated temperatures. Although studies on other materials should be performed, it seems clear that the observed trends are general ones and the grain aspect ratio does not necessarily decrease with temperature.
To maximize the aspect ratio for a given material, the deformation temperature has therefore to be sufficiently high to subdue frequent grain fragmentation by boundary migration, but lower than the temperature where defect annihilation, and so a reduction of the pinning sites for triple junctions, takes place.

Future experiments should be carried out to clarify whether alloying elements or impurities can amplify the observed effect, as it is known that they not only stabilize intragranular defects but also to influence the grain boundary itself. In addition, the possibility to generate nanostructures with different aspect ratios, is expected to allow a thorough evaluation of its effect on mechanical properties.

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