Formation Mechanism of Ultrafine Grained Microstructures: Various Possibilities for Fabricating Bulk Nanostructured Metals and Alloys

Nobuhiro Tsuji1,2, Reza Gholizadeh1, Rintaro Uejī3, Naoya Kamikawa4, Lijia Zhao1,5, Yanzhong Tian1,2,6, Yu Bai1,2 and Akinobu Shibata1,2

1Department of Materials Science and Engineering, Kyoto University, Kyoto, Japan
2Elements Strategy Initiative for Structural Materials (ESISM), Kyoto University, Kyoto 606-8501, Japan
3National Institute for Materials Science (NIMS), Tsukuba 305-0047, Japan
4Department of Mechanical Science and Engineering, Hiroasaki University, Hiroasaki 036-8561, Japan
5ArcelorMittal Global Research and Development, East Chicago, Indiana 46312, USA
6Key Laboratory for Anisotropy and Texture of Materials, School of Materials Science and Engineering, Northeastern University, Shenyang 110819, China

Severe plastic deformation (SPD) have had a revolutionary impact in fabricating ultrafine grained (UFG) or nanostructured metallic materials with bulky dimensions. It is, however, difficult to understand from a viewpoint of conventional metallurgy why UFG microstructures form in the as-deformed (as-SPD-processed) state without annealing process. The mechanism of UFG evolution has not yet been perfectly recognized and even some confusions have been induced. Experimental results of systematic observations on the evolution of microstructures during SPD were introduced in the present manuscript, and it was concluded from the results that the formation of UFG microstructures during SPD could be understood in terms of the grain subdivision mechanism. Consequently, the UFG microstructures formed by SPD have the deformed (strain-hardened) characteristics, which influence their mechanical properties. Besides the breakthrough in grain refinement, some features of SPD processes have become barriers for practical applications of UFG materials and scaling-up of the processes. Several new processes combining phase transformation with plastic deformation were introduced for fabricating UFG microstructures without huge plastic strains, and UFG microstructures successfully obtained by the new processes were shown. Finally, recent finding of fully recrystallized UFG microstructures in some alloys having average grain sizes of several hundred nanometers was exhibited. The fully recrystallized UFG metals all showed both high strength and large ductility, because of the capability of strain hardening in the structures. These recent results are expected to open great possibilities of UFG or nanostructured metals as advanced structural materials. [doi:10.2320/matertrans.MF201936]

Keywords: severe plastic deformation, microstructure evolution, grain subdivision, deformation microstructure, recrystallization, phase transformation, strain hardening, mechanical property

1. Introduction

Almost all structural metallic materials with bulky shapes are polycrystalline materials composed of numerous number of crystal grains. It has been well known that strength and toughness of polycrystalline metals are improved with decreasing the grain size. Concerning the strength, Hall-Petch relationship was empirically found in the form,

$$\sigma_f = \sigma_0 + kd^{-1/2}$$

(1)

where $\sigma_f$ is the yield strength of the polycrystalline material, $\sigma_0$ the friction stress, $k$ the Hall-Petch constant, and $d$ the average grain size.\(^{1,2}\) However, the minimum average grain size in commercial metallic materials with bulky dimensions has been about 10 μm even now. That is, 10 μm has been the limitation of grain refinement for a long period, which means that there remains a large possibility in grain refinement for enhancing properties of metals. Since the end of 1980’s, ultrafine grained (UFG) metallic materials having average grain sizes much smaller than 1 μm have been energetically studied all over the world, where severe plastic deformation (SPD) gave a great breakthrough.\(^{3-6}\) It was found that UFG microstructures could be formed after plastic deformation to very high strains (i.e., SPD). Various kinds of unique SPD processes have been developed for grain refinement,\(^{4,5}\) and superior and sometimes unusual mechanical properties of UFG metals have been clarified.\(^{3-6}\)

On the other hand, it is still unclear why UFG microstructures can be formed by SPD. Conventionally, recrystallization phenomenon happening during annealing after plastic deformation is the major way to refine the grain size of metallic materials.\(^{7}\) However, SPD processes are carried out at relatively low temperatures below recrystallization temperature of the materials in order to effectively accumulate lattice defects introduced by plastic deformation, and UFG microstructures are obtained in the as-SPD-processed state (or the as-deformed state) without annealing treatments. Figure 1 shows transmission electron microscopy (TEM) microstructures of a pure aluminum with 99.99 mass% purity (4N-Al) processed by equal-channel angular pressing (ECAP) at room temperature (RT), reported by Iwahashi et al.\(^{8}\) In the as-deformed state of 4-pass ECAP using a 90° angle die, an UFG microstructure with equiaxed morphology is clearly observed. The question is how and by what mechanism this UFG structure was formed. In beginning of the present overview paper, the authors try to explain the formation mechanism of UFG microstructures in SPD processes, based on their experimental results.

SPD processes are revolutionary for realizing bulky UFG materials, but SPD concept and special techniques for conducting SPD may be strong barriers in considering practical applications of UFG metals. For example, steel industries use enormous facilities, so that it is quite difficult to quickly replace the facilities. SPD processes often involve
difficulties for practical applications, such as discontinuous (batch) nature of the process, complicated procedures, huge working force in scaling-up, durability of dies and tools necessary for SPD, fracture of materials during processing, etc. In the later part of the present overview, we would like to introduce possibilities to fabricate UFG microstructures without SPD or huge plastic strains based on understanding of the mechanism of UFG formation. Additionally, possibilities of fully recrystallized UFG metals recently found are discussed.

2. Formation of Ultrafine Grains during Severe Plastic Deformation

In order to understand the microstructure evolution during SPD, deformation microstructures were tracked by detailed microstructural observations using TEM and electron backscattering diffraction (EBSD) analysis in scanning electron microscope equipped with a field-emission type electron gun (FE-SEM). Ultra-low carbon interstitial free (IF) steel sheets having a polygonal ferrite microstructure (mean grain size: 27 µm) was deformed by accumulative roll bonding (ARB) process. The ARB is a SPD process using rolling deformation. As rolling is the most advantageous metal working process for continuous production of bulky metals in shapes of plates, sheets, bars and so on, the ARB is considered as the most probable SPD process for applying to mass-production of UFG metallic materials. Indeed the concept of ARB has been already used for producing UFG stainless steel thin sheets with thickness of ~0.1 mm, although adaption of the ARB process to large-scale production of UFG materials has not yet been achieved due to the reason mentioned above. In the present experiment in laboratory, the ARB process using 50% reduction in thickness per cycle was applied to the IF steel sheets up to 7 cycles (von Mises equivalent rolling strain (ε) of 7.2). Roll-bonding was carried out at 500°C for achieving good bonding, by the use of a two-high rolling mill with a roll diameter of 310 mm. Two sheets of the IF steel 1 mm thick were stacked after surface treatments, held in a furnace set at 500°C for 600 s, and then roll-bonded by 50% reduction in one pass. The roll-bonded sheets were immediately cooled into water, cut into two pieces, and then provided to the next ARB cycle. Microstructural observations were carried out for the specimens ARB processed to various cycles (i.e., various total strains).

Fig. 2(a) shows a TEM micrograph of the IF steel ARB processed to only 1 cycle (ε = 0.8) at 500°C. The microstructure was observed from TD. The misorientation map was obtained from Kikuchi-line analysis in TEM.

Fig. 2(b) represents the obtained boundary misorientation map of the area shown in Fig. 2(a), where misorientation angles are indicated in degrees. In boundary misorientation maps hereafter, high-angle grain boundaries (HAGBs) with misorientation angles (θ) larger than 15 degrees (θ ≥ 15°) are drawn in green lines, while low-angle grain boundaries (LAGBs) with misorientation
angles smaller than 15 degrees ($\theta < 15^\circ$) are drawn in red lines. The boundary map clearly indicates that most of the boundaries in the sub-grain structure are LAGBs having very small misorientation angles. There are a few HAGBs with large misorientation angles ($\geq 40^\circ$), but they are probably segments of initial grain boundaries involved in this observation area. The microstructure shown in Fig. 2 is a typical deformation microstructure after conventional rolling strains.

Figure 3 shows a TEM image and corresponding misorientation map obtained by the Kikuchi-line analysis of the IF steel ARB processed by 3 cycles ($\varepsilon = 2.4$) at 500°C. The microstructure was observed from TD. The misorientation map was obtained from Kikuchi-line analysis in TEM.\(^{17}\)

Angle plots smaller than 15 degrees are drawn in red lines. The boundary map clearly indicates that most of the boundaries in the sub-grain structure are LAGBs having very small misorientation angles. There are a few HAGBs with large misorientation angles ($\geq 40^\circ$), but they are probably segments of initial grain boundaries involved in this observation area. The microstructure shown in Fig. 2 is a typical deformation microstructure after conventional rolling strains.

Figure 3 shows a TEM image and corresponding misorientation map obtained by the Kikuchi-line analysis of the IF steel ARB processed by 3 cycles ($\varepsilon = 2.4$).\(^{17}\) The microstructure (Fig. 3(a)) is composed of lamella-like sub-grains elongated to the rolling direction (RD) and dislocation cells with undefined morphologies. This still looks like a deformed microstructure, but the misorientation map (Fig. 3(b)) represents different features from that of the specimen ARB processed by 1 cycle (Fig. 2(b)). In addition to a number of LAGBs (red boundaries), clusters of HAGBs (green boundaries) are recognized in Fig. 3(b). The misorientation angles of the HAGBs are fairly high and often over 50°. It is noteworthy that the HAGBs and LAGBs correspond well to the lamellar (sub-)grains and undefined dislocation cells, respectively, in the TEM image (Fig. 3(a)). The average interval of all kinds of observed boundaries along ND is 3.4 µm at this stage, which is much larger than the measured interval of the observed boundaries (0.27 µm). This fact indicates that most of the grain boundaries observed in Fig. 3 (especially most of the lamellar HAGBs) are the boundaries newly introduced by plastic deformation.

Similar TEM observations with Kikuchi-line analysis revealed that the number and fraction of HAGBs increased with increasing the total strain (the number of ARB cycle) applied. TEM image and corresponding boundary misorientation map of the specimen ARB processed by 7 cycles ($\varepsilon = 5.6$) are shown in Fig. 4.\(^{14}\) The microstructure became more homogeneous throughout the specimen, and grains elongated to RD were observed (Fig. 4(a)). Grain boundaries surrounding elongated grains looked sharp, and the mean interval of boundaries along ND (the mean grain thickness) was 0.20 µm. The misorientation map (Fig. 4(b)) indicates that most of the boundaries observed in this microstructure are HAGBs with quite large misorientation angles. This is a typical UFG microstructure fabricated by the ARB process or other SPD processes using monotonic deformation.

More macroscopic views of the microstructure evolution during SPD were observed by EBSD in FE-SEM. Figure 5 represents grain boundary maps obtained by the EBSD analysis of the IF steel ARB processed by various cycles at 500°C. The microstructures were observed from TD, and HAGBs ($\theta \geq 15^\circ$) and LAGBs ($2^\circ \leq \theta < 15^\circ$) were drawn by bold black lines and narrow grey lines, respectively, in this figure. In the EBSD boundary maps, boundaries with very low misorientation angles ($\theta < 2^\circ$) were removed to avoid inaccuracy in EBSD measurement and analysis. The specimen ARB processed by only 1 cycle (50% rolling reduction, $\varepsilon = 0.8$) showed the elongated grains including several
LAGBs (Fig. 5(a)), which were initial grains elongated by 50% rolling and dislocation substructures inside the initial grains, respectively. After 3 cycles of the ARB (Fig. 5(b), \(\varepsilon = 2.4\)), initial grains are furthermore elongated to RD, but fine regions (grains) surrounded by HAGBs are also observed especially near initial grain boundaries. Those fine grains correspond to the fine lamellar grains with HAGBs observed in TEM at this stage (Fig. 3(b)). The number and fraction of fine grains increased with increasing the total strain (the number of ARB cycle) applied (Fig. 5(c)), and finally the lamellar UFG structure composed of elongated grains uniformly formed in the sheet after 7 cycles of the ARB (Fig. 5(d)). Most of the boundaries observed in Fig. 5(d) are HAGBs, which coincides well with the result of local observation by TEM shown in Fig. 4. These are typical processes of microstructure evolution during ARB. EBSD grain boundary maps for a commercial purity aluminum with 99 mass% purity (2N-Al) ARB processed to different cycles (different strains) at RT are shown in Fig. 6, where HAGBs and LAGBs are drawn in green and red lines, respectively. The evolution process of fine-grained microstructures during SPD (ARB) of the 2N-Al was basically the same as that in the IF steel shown in Fig. 5.

3. Formation Mechanism of Ultrafine Grains

The formation process of UFG microstructures during ARB (monotonic SPD process) was experimentally shown in the former section. We think that the observed microstructure evolution can be understood in a context of the development of deformation microstructures. Hansen and co-workers have studied the development of deformation microstructures in metals and alloys for a long period. They call the formation process of deformation microstructures the grain subdivision, which is schematically illustrated in Fig. 7. Within grains in polycrystalline materials, not only the primary slip system having the highest resolved shear stress (the largest Schmid factor for the given macroscopic
stress state) but also other slip systems are activated owing to the constraint by neighboring grains. The straight lines in Fig. 7(a) illustrate slip lines, and the difference in the combination of the slip lines indicates different slip patterns (the amount and combination of activated slip systems) in different areas within an identical grain. The difference in slip patterns causes different crystal rotations at different local areas, leading to the evolution of misorientation between neighboring areas showing different slip patterns. Such misorientation angles are borne by the Geometrically Necessary Boundaries (GNBs),20–22) which are dislocation boundaries with planar morphologies introduced by plastic deformation (Fig. 7(b)). Many dislocations are also stored within each domain divided by GNBs, and they tend to form low-energy configurations. Dislocation boundaries formed in such a way are named Incidental Dislocation Boundaries (IDBs).20–22) Typical example of IDBs is dislocation cell boundaries in deformed microstructures. When deformed microstructures are observed at different stages of plastic deformation, one can see that original grains are subdivided by GNBs and IDBs (Fig. 7(b)), which is called the grain subdivision. The grain subdivision progresses with increasing the total plastic strain, and initial crystals are more and more finely subdivided (Fig. 7(c)). It has been experimentally found that the density and the misorientation angles of GNBs monotonously increases with increasing the applied plastic strain and GNBs become even HAGBs,19,21) while the misorientation angle of IDBs does not increase so much and IDBs stay as LAGBs.21) In conventional tension/compression tests and metal working processes to relatively small plastic strains, however, the number and density of GNBs having very high misorientation angles are limited. When quite high plastic strains are applied in monotonic manner to the material, lamellar boundary structures illustrated in Fig. 7(d) form. The microstructure involves relatively high density of GNBs with lamellar morphologies (lamellar boundaries) having large misorientation angles. Figure 8 shows typical TEM images of deformed microstructures in 2N-Al.21,23) A channel structure constructed by straight GNBs is seen in the 2N-Al cold-rolled by 10% reduction (ε = 0.12), as shown in Fig. 8(a). There are dislocation cells (IDBs) within rectangular regions subdivided by GNBs (Fig. 8(a)). On the other hand, a lamellar boundary structure elongated to RD is observed in the 2N-Al heavily cold-rolled by 99.3% reduction (ε = 5.6), as shown in Fig. 8(b). It was reported that the lamellar boundary structure shown in Fig. 8(b) includes relatively large fraction of HAGBs (high-angle GNBs).23) TEM microstructures of the IF steel and the 2N-Al ARB processed by 6 cycles (ε = 4.8) are shown in Fig. 9(a) and
grained structures having larger amount of HAGBs formed in the ARB processed materials than in the cold-rolled materials after equivalent total strains.25 This was explained by the redundant shear deformation introduced by the large one-pass rolling under high friction conditions in the ARB process.27–29

The authors think that the grain subdivision is the common mechanism for the formation of ultrafine microstructures in ultra-heavy deformation (in any types of SPD). However, the formation process is sometimes called in different terminology, such as grain fragmentation, in-situ recrystallization, continuous dynamic recrystallization, etc. Especially when the deformation is carried out at relatively high temperatures, restoration processes may occur during or after the deformation. Even when the deformation is carried out at ambient temperature, restoration can occur more or less, especially in materials with relatively low melting-point temperature. Furthermore, SPD using large one-pass deformation often induces a temperature increase of materials (at least in local areas) due to adiabatic heating. For understanding the effect of restoration, it is necessary to investigate the effect of deformation temperature and strain rate on the microstructure evolution. However, the effect of temperature and strain rate in SPD has not yet been studied, because in most SPD processes it is difficult to carry out continuous SPD at a constant temperature and strain rate.

Recently, Gholizadeh et al.30 have carried out systematic investigations of continuous SPD for various kinds of metallic materials at different temperatures and strain rates by the use of a simple torsion machine equipped with induction heating system. Figure 10 shows the result of such torsion experiments, where IF steel specimens were continuously deformed to high strains up to von Mises equivalent strain ($\varepsilon$) of 7.0 at various constant temperatures ranging from 400°C to 850°C and various constant strain rates from 0.01 s$^{-1}$ to 1 s$^{-1}$. The IF steel specimens were quenched into water immediately after the torsion deformation, and frozen microstructures were analyzed in detail.30 Figure 10(a) exhibits relationships between the obtained grain/sub-grain sizes and the flow stress in the torsion deformation. The grain/sub-grain sizes showed certain correlations with the flow stress, but there were three different regions in the change of the grain size determined as the interval of HAGBs. Typical microstructures (EBSD grain boundary maps) in three regions are shown in Fig. 10(b), (c), and (d). In the region of high flow stresses, ultrafine lamellar structures (type I) were mainly observed. This type of microstructure is quite similar to the lamellar UFG structures formed by SPD (ARB) of IF steel shown in Fig. 5(d) and Fig. 9(a), which suggests that the type I structures (Fig. 10(b)) are formed by the grain subdivision mechanism. In fact, the sizes of sub-grains (a kind of deformed microstructures formed by plastic deformation) were on the identical straight line of the grain size determined by HAGBs in the high-stress region, suggesting the same formation mechanism. In the transition region under medium flow stresses, morphologies of fine grains changed into more equiaxed ones and the grain size increased with decreasing the flow stress (Fig. 10(c): type II). In the low flow-stress region, heterogeneous microstructures composed of some
coarse grains surrounded by HAGBs within regions of sub-grains with LAGBs were observed (Fig. 10(d): type III). Such microstructures were similar to those formed by dynamic recrystallization (DRX; recrystallization during deformation). The flow stress dependence of the grain size determined by HAGBs in this region had nearly the same slope as that for the sub-grain size, but the grain sizes were much coarser than the sub-grain sizes (or the grain sizes extrapolated from the high flow-stress region).

The results can be summarized in the following way: when the sub-grain size formed by deformation is maintained up to high strains (under high stress conditions at low temperatures or/and at high strain rates), the grain subdivision mechanism would dominate the formation process of UFG microstructures (type I in Fig. 10(b)). In deformation under low flow stress (at high temperatures or/and at low strain rates), recovery inhibits the development of HAGBs by the grain subdivision mechanism, leading to heterogeneous distribution of the regions surrounded by HAGBs (type III in Fig. 10(d)). The regions surrounded by HAGBs heterogeneously distributed within sub-grains with LAGBs would grow due to the high mobility of HAGBs. Consequently the microstructures can be recognized as typical (discontinuous) DRX structures characterized by nucleation and growth of recrystallized regions. When the DRX characterized by grain growth happens, it would be difficult to maintain (ultra-)fine grain sizes. In the transition region, recovery controlled by lattice diffusion is inhibited rather than that under the low flow stress, so that the microstructure evolution is still dominated by the grain subdivision mechanism. However, migration of HAGBs controlled by grain boundary diffusion can happen under this condition, resulting in the relatively fine grains with equiaxed morphologies (type II in Fig. 10(c)). The increase of the grain size from that expected as the result of the grain subdivision mechanism (sub-grain sizes in Fig. 10(a)) is also observed.

Based on the understanding, let us look back the equiaxed UFG structures observed in the pure aluminum SPD (ECAP) processed at RT (Fig. 1). It should be noted firstly that the material used was a high-purity aluminum (4N-Al). For aluminum of which melting point temperature ($T_m$) is 660.3°C (937.3 K), ambient temperature (25°C = 298 K) is relatively a high temperature ($\approx 0.32T_m$). High purity of the material and adiabatic heating during heavy deformation in a small deformation zone at the corner of ECAP die would enhance grain boundary migration (of HAGBs) formed by the deformation. It can be concluded that the equiaxed fine-grained structure shown in Fig. 1 corresponds to the type II microstructure (Fig. 10(c)) in the continuous torsion deformation under medium flow stress conditions. High density of HAGBs in such a type II microstructure is resulted from the grain subdivision, and grain boundary migration changes morphologies of grains from lamellar one to equiaxed one and somewhat coarsens the grain size. The combinations of different processes (i.e., grain subdivision, grain boundary migration and recovery) would determine the grain size obtained by high-strain deformation under given deformation conditions and materials. The grain size saturation that has been reported in various kinds of SPD processed materials could be explained by the combination of the refinement process (grain subdivision) and the coarsening processes (recovery, grain boundary migration, triple junction motion, and so on).

One may point out the effect of strain paths on morphologies and sizes of UFG microstructures formed by SPD, since the equiaxed UFG structure shown in Fig. 1 was fabricated by the route-Bc ECAP process where the bar-specimen was rotated by 90° around the bar axis after every...
pass of the ECAP. In fact, a number of papers reported that different strain paths in SPD changed morphologies and formation speeds of UFG microstructures. The effect of redundant shear strain in ARB mentioned above is also a kind of strain path effects. It is known that the multi-directional (or multi-axial) forging, where macroscopic shapes of materials are kept nearly identical after one-cycle of deformation, tends to exhibit equiaxed UFGs after heavy deformation. The effect of redundant shear strain in ARB mentioned above is also a kind of strain path effects. It is known that the multi-directional (or multi-axial) forging, where macroscopic shapes of materials are kept nearly identical after one-cycle of deformation, tends to exhibit equiaxed UFGs after heavy deformation. The change in microstructure formation by changing the strain path seems reasonable, since the priority orders of slip systems differ under different loading directions (i.e., when the strain path is changed) even within identical grains, which would lead to the change of local slip patterns. This might be termed as the effect of crystallographic texture that is also changed by following different strain paths. Orlov et al. studied the effect of reverse deformation in HPT deformation on microstructures and textures of severely deformed materials. They clearly showed that strain reversal retarded the grain refinement, compared with monotonic HPT deformation to the same amount of plastic strains. It is, on the other hand, noteworthy that when high-purity Al (4N-Al with 99.99 mass% purity) was heavily deformed, equiaxed fine grains formed even in case of monotonic HPT. The equiaxed fine-grain structures they reported are quite similar to that obtained by the route-B2 ECAP process shown in Fig. 1. Zhang et al. studied the microstructural evolution during monotonic HPT at RT for nickel (Ni) having higher melting point and therefore recovery and grain boundary migration are more difficult at RT compared to Al. The Ni specimens showed typical deformation microstructures that can be explained by the grain subdivision mechanism, even though Ni with a purity of 99.99 mass% (4N-Ni) exhibited a more recovered and equiaxed microstructure than 2N-Ni (99 mass% purity) after monotonic HPT up to the same equivalent strain of 100. It is also interesting that microstructures in a 99.5% purity Ni changed from typical lamellar morphologies at a strain of 100 into more equiaxed ones after a strain of 300. The results suggest that the accumulation of lattice defects (probably including vacancies) during quite high plastic deformation would accelerate the coarsening processes (recovery, grain boundary migration, triple junction motion, and so on), leading to nanostructures having more equiaxed morphologies. Anyway, these results indicate that the grain subdivision is primarily the common mechanism for the formation of ultrafine- or nano-structures not only in monotonic SPD but also in general SPD processes including different strain paths.

4. Simpler Ways to Fabricate Ultrafine Grained Metals without Severe Plastic Deformation

SPD can realize UFG microstructures and even nanostructures in most kinds of metals and alloys, unless the materials are fractured during SPD. However, fairly high plastic strains are necessary to form homogeneous UFG and nanostructures. Kamikawa et al. assessed the development of UFG structures in a commercial purity aluminum (2N-Al) ARB processed under unlubricated condition at RT. Figure 11 shows their results, where the average spacing of HAGBs (a) and the fraction of HAGBs (b) in the material are plotted as a function of the total equivalent strain. Since it had been clarified that the redundant shear strain in the unlubricated ARB process accelerate the formation of UFGs, the equivalent strain in Fig. 11 took into account of the redundant shear strain in addition to the rolling strain. The spacing of HAGBs (grain size) quickly decreases and the fraction of HAGBs quickly increases with increasing the equivalent strain applied by the ARB, but both parameters eventually saturate to show constant values. The graphs clearly show that the equivalent strain of 5 or more is required to obtain homogeneous UFG microstructures having high density of HAGBs. In conventional metal working processes, however, it is difficult to achieve the logarithmic equivalent strain over 5, which has been a barrier for large-

![Fig. 11](image_url)
scale practical applications of UFG or nanostructured metals. Therefore, it is beneficial if UFGs could be realized by the processes using less plastic strains, and simpler processes would greatly expand the possibility of nanostructured metals.

Tsuji and Maki\textsuperscript{42} proposed to combine phase transformations with plastic deformation for producing UFG microstructures without huge plastic strains. Besides recrystallization, phase transformation is another phenomenon that can make fine-grained microstructures in metallic materials, and various kinds of phase transformations have been used for grain refinement even in industry scales. Especially, steels have variety of options for grain refinement, since steels show different kinds of phase transformations, such as ferrite transformation, martensitic transformation, bainitic transformation, and so on. Here, several examples of the ways to make UFG microstructures without very high plastic strains are introduced.

Ueji et al.\textsuperscript{43,44} have found a simple route for fabricating nanostructured low-carbon steels without SPD. The point of their process is to use as-quenched martensite as the starting microstructure for deformation. The as-quenched martensite of a 0.13 mass\% C steel was simply cold-rolled only by 50\% reduction in thickness and then annealed at relatively low temperatures where only recovery occurs usually. Figure 12 shows a TEM image and corresponding grain boundary misorientation map obtained by TEM Kikuchi-line analysis of the 0.13\%C steel annealed at 500°C for 1.8 ks after 50\% cold-rolling of martensite starting microstructure. Nearly equiaxed UFGs with an average grain size of 180 nm were observed (Fig. 12(a)). The misorientation map (Fig. 12(b)) clearly indicated that many UFGs were surrounded by HAGBs. Since martensite of carbon steels are supersaturated solid solution of carbon, fine carbides near-homogeneously precipitated within the matrix. Such carbides inhibited grain growth of the ferrite matrix to maintain UFG microstructures, and also enhanced strain-hardening in subsequent deformation due to the constraint of grain boundaries.\textsuperscript{44} However, why was the UFG microstructure easily obtained only after 50\% cold-rolling and annealing? Martensite in low-C steels transforms keeping their process is to use as-quenched martensite as the starting microstructure for deformation. The as-quenched martensite of a 0.13 mass\% C steel was simply cold-rolled only by 50\% reduction in thickness and then annealed at relatively low temperatures where only recovery occurs usually. Figure 12 shows a TEM image and corresponding grain boundary misorientation map obtained by TEM Kikuchi-line analysis of the 0.13\%C steel annealed at 500°C for 1.8 ks after 50\% cold-rolling of martensite starting microstructure. Nearly equiaxed UFGs with an average grain size of 180 nm were observed (Fig. 12(a)). The misorientation map (Fig. 12(b)) clearly indicated that many UFGs were surrounded by HAGBs. Since martensite of carbon steels are supersaturated solid solution of carbon, fine carbides near-homogeneously precipitated within the matrix. Such carbides inhibited grain growth of the ferrite matrix to maintain UFG microstructures, and also enhanced strain-hardening in subsequent deformation due to the constraint of grain boundaries.\textsuperscript{44} However, why was the UFG microstructure easily obtained only after 50\% cold-rolling and annealing? Martensite in low-C steels transforms keeping Kurdjumov-Sachs (K-S) orientation relationship with austenite (mother phase). Assuming the K-S orientation relationship, 24 different variants (24 different orientation) of martensite crystal can crystallographically form within a single crystal (single grain) of austenite. As a result, martensite microstructure is a kind of fine-grained microstructures even in the as-transformed state. Figure 13(a) shows an EBSD orientation map of an as-quenched martensite in a low-C steel (0.2 mass\% C steel).\textsuperscript{45} The white lines were grain boundaries surrounding a prior austenite grain reconstructed from the crystallographic analysis. It could be clearly seen that, within the single austenite grain, a number of different variants of martensite (painted in different colors and indicated as “V2”, “V14”, etc.) formed. A grain boundary map corresponding to the area shown in Fig. 13(a) is represented in Fig. 13(b). Boundaries existing in the microstructure are categorized into three kinds depending on their misorientation angles and drawn in different colors. It was recognized that the original austenite grains were finely subdivided by the martensitic transformation. The effective grain size of this martensite microstructure estimated from HAGBs was approximately 1 \mu m. Since the starting martensite structure had such a fine-grained microstructure with a high density of grain boundaries already, it was considered that the grain subdivision process in cold-rolling was accelerated due to the constraint of grain boundaries. It should be also noted that the as-quenched martensite involved a high density of dislocations. These were probably the reason why only 50\% cold-rolling and subsequent recovery annealing could produce the UFG microstructure. The TEM microstructure of the 50\% cold-rolled specimen (Fig. 13(c)) revealed a complicated deformation microstructure. Ultrafine lamellar structures were observed in most areas, and they had wavy shapes due to additional shear localization. Selected area diffraction patterns suggested the existence of local misorientations. That is, the finely subdivided structure comparable to those formed after SPD was prepared by the grain subdivision only after 50\% cold-rolling of martensite. This is an example of the simple processes to fabricate UFG microstructures without SPD. Firstly, the phase transformation (martensitic transformation) made the appropriate starting microstructure, and then plastic deformation (conventional cold-rolling) and subsequent annealing realized the UFG microstructure shown in Fig. 12.

Okitu et al.\textsuperscript{46} showed another example of the simple processes, using a 0.10C–1.98Mn–0.018Nb–0.0015B (mass\%) steel. They firstly made a dual phase microstructure composed of ferrite (F) and martensite (M) shown in Fig. 14(b) through conventional hot-rolling, air cooling, and quenching from ferrite + austenite two-phase temperatures (Fig. 14(a)). Figure 14(c) represents a SEM image observed from TD of the as 91\% cold-rolled specimen having...
Fig. 13  (a) EBSD orientation color map showing variant distribution and (b) grain boundary map of the same area of the as-quenched lath martensite in a 0.20% C steel.\(^{45}\) (c) TEM microstructure observed from TD of the 50% cold-rolled martensite of a 0.13% C steel.\(^ {43}\)

Fig. 14  (a) Thermo-mechanical treatments applied to a 0.10C–1.98Mn–0.018Nb–0.0015B (mass%) steel for obtaining UFG microstructures. (b) SEM micrograph of the starting microstructure for subsequent cold-rolling, which shows a dual-phase microstructure composed of ferrite (F) and martensite (M) formed by quenching from austenite + ferrite two-phase temperature after hot-rolling. (c) SEM micrograph showing the 91% cold-rolled microstructure. (d) EBSD grain boundary map of the specimen 91% cold-rolled and then annealed at 620°C for 120 s.\(^ {46}\)
the dual phase starting microstructure. Since martensite was much harder than ferrite, plastic deformation was concentrated in soft ferrite, and hard martensite was not heavily deformed and showed an island morphology with diamond shapes. Consequently, it is supposed that ferrite regions had deformation microstructures comparable to SPD processed ones (like Figs. 4 and 9), even though the total rolling reduction was not huge (91%, $\varepsilon = 2.8$). Although the degree of deformation in martensite was much smaller than that in ferrite, it was shown by Ueji et al.\textsuperscript{43,45} that smaller amount of strain was enough to finely subdivide as-quenched martensite (Fig. 13). As a result, homogeneous UFG structures having equiaxed morphologies like Fig. 14(d) could be obtained after annealing the 91% cold-rolled sheet under appropriate conditions. The equiaxed microstructure having a mean grain size of 490 nm shown in Fig. 14(d) is considered to be a kind of statically recrystallized microstructure similar to the type II microstructure shown in Fig. 10(c). In this case, again, the first transformation produced the appropriate starting microstructure (the dual phase microstructure of ferrite and martensite), and subsequent cold-rolling and annealing realized the UFG microstructure without SPD.

Combining two processes in the sequence of plastic deformation first and then phase transformation has been used in steel industries, and so-called “controlled rolling” to produce thick plates for welded structures is the most successful example.\textsuperscript{47} In the controlled-rolling, hot-rolling of plates is finished at relatively low temperatures. During multi-pass hot-rolling, austenite grains are refined by deformation and recrystallization process, but recrystallized grains easily grow at high temperatures. In the controlled rolling, small amounts of carbide/nitride forming elements, such as Nb and Ti, are added to the steel, and ingots are soaked at higher temperature to dissolve these alloying elements in solution. With lowering the hot-rolling temperature, these elements finely precipitate as carbides and nitrides in deformed microstructures, and the carbides and nitrides inhibit recovery and recrystallization to maintain deformation microstructures of austenite even after the hot-rolling process. The deformation microstructures and dislocations within austenite grains, as well as grain boundaries of austenite, act as high-density nucleation sites for subsequent ferrite transformation. As a result, fine-grained ferrite microstructures with average grain size down to 5 $\mu$m could be realized in thick plates, which realized high strength and high toughness keeping good weldability.\textsuperscript{47} Progress of rolling mill machines nowadays enables to reduce finishing temperature of hot-rolling process furthermore and to increase one-pass reduction in finishing rolling. Consequently, UFG ferrite grains with grain sizes smaller than 1 $\mu$m have been sometimes reported through physical simulation of such processes in laboratory scales.\textsuperscript{48–50} However, the formation mechanism of UFG ferrite microstructures in such high temperature processes is still unclear.

When large rolling reduction is applied at relatively low temperatures in the hot-rolling process, the plastic deformation significantly accelerates the kinetics of ferrite transformation. As a result, ferrite transformation might happen during deformation under certain conditions. The transformation happening during deformation is called dynamic transformation (DT), and the occurrence of DT has been confirmed by some experimental studies under particular conditions.\textsuperscript{51–55} Recently, Zhao et al.\textsuperscript{50,56} have found that two different mechanisms happen sequentially in certain materials and hot-deformation conditions, resulting to form UFG microstructures. Figure 15(a) schematically illustrates the mechanisms.\textsuperscript{56,57} When austenite ($\gamma$) is hot-deformed at supercooled temperatures under certain deformation conditions, DT to ferrite ($\alpha$) occurs to form relatively fine ferrite microstructures. Although the DT ferrite grow after nucleation, they then show DRX during continuous deformation. After such understanding, a thermo-mechanically controlled process under designed multi-step conditions realized UFG ferrite microstructures in a 10Ni–0.1C (mass%) steel, as shown in Fig. 15(b) and (c). Figure 15(b) and (c) are EBSD grain boundary map and TEM image of the obtained UFG microstructure, respectively. The GB map clearly showed an uniform UFG structure composed of ultrafine ferrite grains with nearly equiaxed morphologies. The average grain size of the ultrafine ferrite was 0.55 $\mu$m. The TEM image confirmed the existence of dislocations within UFGs, which could be the evidence of DRX occurring during plastic deformation. This is another example of the simple processes combining plastic deformation and phase transformation to fabricate UFG microstructures.

It can be concluded that there are still wide possibilities of simple processes without huge plastic strains, for fabricating UFG or nanostructured bulky metallic materials, especially in steels showing variety of phase transformations. It is noteworthy that all UFG steels obtained by the new processes introduced above performed both high strength and good tensile ductility,\textsuperscript{43–57} possibly because the microstructures had more or less recrystallized nature.

5. Fully Recrystallized Ultrafine Grained Metals

SPD can fabricate UFG microstructures in various kinds of metallic materials. The UFG materials fabricated by SPD processes show very high strength, but their tensile ductility is usually limited. One of the reasons for the limited tensile ductility (especially the limited uniform elongation) is early plastic instability caused by the high yield strength and the limited strain-hardening capability in the obtained nanostructures.\textsuperscript{58,59} Additionally, deformed characteristics in as-SPD processed nanostructures must be harmful for the ductility. It has been well known that even in conventional metal working processes strain-hardened metals always show limited tensile ductility (uniform elongation), because yield strength is increased by plastic deformation and capacity of strain-hardening is already limited in strain-hardened materials. We have shown in the former section that the mechanism of grain refinement in SPD is the grain subdivision. Naturally, UFG microstructures fabricated by SPD have strain-hardened nature: elongated grain morphologies and high dislocation densities within grains. Limited tensile ductility of as-SPD-processed materials must be, therefore, unavoidable.

In conventional metallurgy, strain-hardened materials are annealed at elevated temperatures to recover their ductility
and formability (i.e., to soften the materials). During annealing heat-treatments, recovery, recrystallization and grain growth phenomena may happen, and increase of ductility is mainly given by recrystallization. Annealing treatments have been also applied to SPD materials, and ductility could be improved in fact. However, in many cases, the grain size of the annealed materials increased above one ~ several micro-meters after recrystallization happened or ductility recovered, so that the advantages of UFG microstructures, such as high strength, were already lost. On the other hand, it has been found recently that fully recrystallized UFG structures keeping sub-micrometer grain sizes could be realized in particular alloys. For example, Saha et al. found a fully recrystallized UFG structure with an average grain size of 400 nm after annealing 30Mn–3Al–3Si (mass%) steel cold-rolled to 92%. The 30Mn–3Al–3Si steel is an austenitic steel having face centered cubic (FCC) structure at room temperature, and one of the so-called TWIP (twinning induced plasticity) steels because of their high strength and large ductility probably caused by deformation twinning. Then, Tian et al. applied this finding to high-strength TWIP steel (Fe–22Mn–0.6C; mass%) and succeeded in obtaining fully recrystallized UFG microstructures in this steel, too. An example of the fully recrystallized UFG structures in the 22Mn–0.6C steel is shown in Fig. 16. Figure 16(a) and (b) are EBSD orientation color map and grain boundary map of the same area of the fully recrystallized UFG structure. The grain sizes were fairly uniform, and the average grain size of this microstructure was 580 nm. Table 1 summarizes fully recrystallized UFG microstructures in several kinds of alloys reported by now. It is noteworthy that many of them are FCC alloys having low stacking fault energies. Mg–6.2Zn–0.5Zr–0.2Ca (in mass%) alloy has hexagonal close packed (HC) crystal structure, but it includes a high density of fine precipitates in the microstructure, which can inhibit grain growth of the matrix to maintain ultrafine recrystallized grain sizes. It should be emphasized that all these materials having fully recrystallized UFG structures managed both high strength and large tensile ductility. Figure 16(c) shows engineering stress-strain curves of the 22Mn–0.6C steel having two different average grain sizes, 21 µm and 0.58 µm (580 nm). The yield strength of the specimen with 0.58 µm grain size was much higher than that of the 21 µm specimen. This is quite preferable, since the low yield strength is one of the disadvantages of TWIP steels having FCC structure. It should be noted that the 0.58 µm specimen still showed good strain-hardening in spite of the high yield strength, which resulted in large tensile elongation (large uniform elongation) of about 60% by avoiding early plastic instability. The fact that all UFG materials having fully recrystallized morphologies showed large strain-hardening capability even after yielding at high stresses (and then both high strength and large tensile ductility) suggested that strain-hardening mechanism might change in the fully recrystallized UFG microstructures. It can be, anyway, concluded now that fully
Fig. 16 (a) EBSD orientation color map and (b) grain boundary map of the 22Mn-0.6C annealed at 550°C for 240 s after the repeated cold-rolling and annealing process. (c) Engineering stress-strain curves of the 22Mn-0.6C steel having average grain sizes of 21 µm and 580 nm. Obtained by tensile tests at RT.

Table 1 Summary of fully recrystallized ultrafine grained microstructures reported in various kinds of alloys.

<table>
<thead>
<tr>
<th>Alloy (mass%) (Structure)</th>
<th>Process</th>
<th>Minimum Average Grain Size</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-31Mn-3Al-3Si (FCC)</td>
<td>92% cold-rolled + annealed at 650°C for 300 s</td>
<td>400 nm</td>
<td>[60]</td>
</tr>
<tr>
<td>Fe-22Mn-0.6C (FCC)</td>
<td>Repeated cold-rolling and annealing + final annealing at 550°C for 240 s</td>
<td>550 nm</td>
<td>[61]</td>
</tr>
<tr>
<td>Fe-22Mn-0.6C (FCC)</td>
<td>Repeated cold-rolling and annealing + final annealing at 550°C for 300 s</td>
<td>580 nm</td>
<td>[68]</td>
</tr>
<tr>
<td>Cu-15at%Al (FCC)</td>
<td>96% cold-rolled + annealed at 400°C for 40 min</td>
<td>600 nm</td>
<td>[62]</td>
</tr>
<tr>
<td>Cu-10.8at%Al (4.9mass%Al) (FCC)</td>
<td>90% cold-rolled + annealed</td>
<td>470 nm</td>
<td>[63]</td>
</tr>
<tr>
<td>CoCrNi equi-atomic alloy (FCC)</td>
<td>HPT by 5 rotations + annealed at 700°C for 1.8 ks</td>
<td>199 nm</td>
<td>[65]</td>
</tr>
<tr>
<td>Fe-24Ni-0.3C (FCC, metastable)</td>
<td>HPT 5 rotations + annealed (austenitized) at 530°C for 600 s</td>
<td>420 nm</td>
<td>[67]</td>
</tr>
<tr>
<td>Cu-7Ag-0.05Zr (FCC with fine precipitates)</td>
<td>HPT 10 rotations + annealed at 350°C for 300 s</td>
<td>117 nm</td>
<td>[66]</td>
</tr>
<tr>
<td>Mg-6.22Zn-0.5Zr-0.2Ca (HCP with fine precipitates)</td>
<td>HPT by 1 rotation + annealed at 300°C for 60 s</td>
<td>770 nm</td>
<td>[64]</td>
</tr>
</tbody>
</table>
recrystallized nanostructured metals have significant possibilities as the advanced UFG materials managing both high strength and large ductility/formability.

6. Summary

The present overview paper discussed and summarized the mechanisms and processes for the formation of ultrafine grained (UFG) microstructures in bulky metallic materials. Main conclusions are as follows.

1. The evolution of ultrafine grained microstructures in severe plastic deformation (SPD) can be understood in terms of the grain subdivision mechanism which is clearly distinguished from classical recrystallization phenomenon in deformed materials. As a result, the UFG microstructures obtained by SPD have the deformed (or strain-hardened) characteristics which affect their mechanical properties.

2. Combining phase transformation with plastic deformation can be an alternative way to fabricate UFG metals without huge plastic strains. Especially in steels, simple processes using the unique starting microstructures for accelerating the grain subdivision mechanism, and the dynamic transformation followed by dynamic recrystallization mechanisms at elevated temperatures have succeeded in realizing UFG microstructures without huge plastic strains.

3. Fully recrystallized UFG microstructures with average grain sizes of several hundred nano-meters have been recently realized in some kinds of alloys, even through conventional heavy rolling and annealing. It is noteworthy that the fully recrystallized UFG metals show good strain-hardening capability after yielding at high stress level, which leads to managing both high strength and large tensile ductility.

Acknowledgement

This study was financially supported by the Elements Strategy Initiative for Structural Materials (ESISISM), the Grant-in-Aid for Scientific Research (S) (No. 15H05767), and the Grant-in-Aid for Scientific Research on Priority Area on High Entropy Alloys (No. 18H05455), all through the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. NT was also supported by the Light Metal Educational Foundation. All the supports are gratefully appreciated.

REFERENCES


47) I. Kozasa: Controlled Rolling, Controlled Cooling, (Iron and Steel