Advances in ultrafine-grained materials

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This review addresses new developments in the processing and properties of ultrafine-grained (UFG) materials. These materials are produced through the application of severe plastic deformation to conventional coarse-grained metals and typically they have grain sizes within the submicrometer or even the nanometer range. Although several techniques are now available for achieving excellent homogeneity and high fractions of high-angle grain boundaries, this review concentrates on the major procedures of equal-channel angular pressing and high-pressure torsion. It is shown that UFG materials exhibit both excellent strength at ambient temperature and, if the grains are reasonably stable, outstanding superplastic properties at elevated temperatures. These materials also have a high innovation potential for use in commercial applications.

Introduction

It is now well known that the grain size is the major microstructural parameter in dictating the properties of a polycrystalline material. The precise significance of the grain size is dependent upon two relationships that are applicable at either low or high operating temperatures, respectively.

At low temperatures, the strength generally follows the Hall–Petch relationship\cite{1,2} so that
\begin{equation}
\sigma_y = \sigma_o + k_yd^{-1/2}
\end{equation}
where \(\sigma_y\) is the yield stress, \(\sigma_o\) is the lattice friction stress, \(k_y\) is a constant of yielding and \(d\) is the grain size. Thus, the strength of the material increases when the grain size is reduced. At high temperatures and under conditions of constant stress or load, the steady-state strain rate, \(\dot{\varepsilon}\), is given by a relationship of the form\cite{3,4}
\begin{equation}
\dot{\varepsilon} = \frac{ADGb}{kT}\left(\frac{b}{d}\right)^p\left(\frac{\sigma}{G}\right)^n
\end{equation}
where \(D\) is the appropriate diffusion coefficient (=\(D_o\exp(-Q/RT)\)), \(D_o\) is a frequency factor, \(Q\) is the activation energy, \(R\) is the gas constant and \(T\) is the absolute temperature, \(G\) is the shear modulus, \(b\) is the Burgers vector, \(k\) is Boltzmann’s constant, \(\sigma\) is the applied stress, \(p\) and \(n\) are the exponents of the inverse grain size and the stress, respectively, and \(A\) is a dimensionless constant. For coarse-grained materials the flow processes at elevated temperatures are intragranular in nature and \(p = 0\) but when the grain size is reduced other flow processes become important which are dependent on the grain size\cite{5} such as Nabarro–Herring\cite{6,7} and Coble\cite{8} diffusion creep and superplasticity. The high ductilities occurring in superplastic flow are due to grain boundary sliding\cite{9} combined with accommodation by limited intragranular slip to prevent the development of internal cavities\cite{10–13}. For grain boundary sliding in superplasticity, theory predicts\cite{14} that flow follows Eq. (2) with \(p = 2, n = 2, D = D_gb\) where \(D_gb\) is the coefficient for grain boundary diffusion and \(A \approx 10\). Thus, grain refinement provides an opportunity for achieving superplastic elongations at elevated temperatures provided the small grains have reasonable thermal stability. Furthermore, because the strain rate is dependent upon the reciprocal of the grain size raised to a power of \(p = 2\), it follows that a reduction in grain size leads to the occurrence of superplasticity at faster strain rates.

The potential for achieving high strength at ambient temperature and a superplastic flow capability at elevated temperatures is very attractive. Currently, the commercial superplastic forming
industry fabricates thousands of tons of metallic parts every year through the superplastic forming of sheet metals [15] but the basic materials are produced through thermo-mechanical processing and the grain sizes are typically in the range of $\sim 5 \text{ to } 10 \mu m$. In practice, it is generally not possible to use thermo-mechanical processing to produce metals with grain sizes smaller than $1 \mu m$ although a reduction in grain size holds the promise of easier and faster forming operations.

**Methods for producing ultrafine-grained (UFG) materials**

Metals having grain sizes smaller than $1 \mu m$ may be produced in two fundamentally different ways [16]. The first procedure, known as the “bottom-up” approach, assembles polycrystalline metals from individual atoms using deposition techniques or from nanoscale building blocks produced, for example, by high-energy ball milling. However, there are fundamental disadvantages with these techniques because the samples are very small, they contain at least a small amount of residual porosity and they are suitable primarily for use only in micro-devices. The second procedure is the “top-down” approach in which bulk fully-dense coarse-grained polycrystalline solids are processed by severe plastic deformation (SPD) to introduce a high dislocation density without any concomitant change in the cross-sectional dimensions of the specimens. Using this approach, the dislocations are able to re-arrange into arrays of high-angle grain boundaries and the resultant grain sizes are typically in the submicrometer range of 100–1000 nm or even in the true nanometer range of $<100$ nm. Several different SPD procedures are now available [17,18] but to date most attention has been given to the procedures of equal-channel angular pressing [19] (ECAP) and high-pressure torsion [20] (HPT). Of these two procedures, HPT processing is especially attractive because it leads to grains which are generally smaller than those produced using ECAP [21–23].

The processing of metals by ECAP was first developed by Dr. V.M. Segal and co-workers in the 1970s and 1980s at an institute in Minsk in the former Soviet Union (now Belarus) [24]. The original objective was to develop a metal forming process using simple shear but later, in the 1990s, reports appeared describing the potential for using ECAP for the production of UFG materials [25,26].

The general principles of ECAP are depicted schematically in Fig. 1. The processing is conducted using a die containing a channel bent through a sharp angle near the center of the die. The sample billet is machined to fit within the channel and then a plunger is used to press it through the die under an applied pressure $P$. Since the billet is constrained to remain within the channel, it ultimately emerges as shown on the right in Fig. 1. It is readily apparent that, since the cross-sectional dimensions remain unchanged in the pressing operation, repetitive processing may be undertaken in order to impose very high strains. In practice, the strain introduced in each pass of ECAP is dependent upon both the angle $\Phi$ between the two parts of the channel and the angle $\Psi$ representing the outer arc of curvature where the two parts intersect [27]. Calculations show the angle $\Psi$ plays only a minor role for channel angles of $90^\circ$ and higher so that it is reasonable to assume an imposed strain of $\sim 1$ when $\Phi = 90^\circ$ for each separate pass through the die. The angle at the arc of curvature $\Psi$ becomes more important when the channel angle is less than $90^\circ$ as shown by experiments using a die with a channel angle of $60^\circ$ [28]. Fig. 1 also indicates an $X$, $Y$, $Z$ coordinate system which can be used when processing by ECAP.

Processing by HPT has a longer history than ECAP and dates back to the work of Nobel Laureate Professor P.W. Bridgman conducted at Harvard University in the 1930s and 1940s [29,30]. Nevertheless, it was only much later, with the advent of sophisticated instruments for analytical microscopy, that HPT processing was recognized as a tool that may be used to introduce exceptional grain refinement into polycrystalline solids [31].

The principle of processing by HPT is illustrated schematically in Fig. 2 [32]. The sample is generally in the form of a thin disk and it is placed between two massive anvils, subjected to a pressure $P$ and then torsionally strained through rotation of either the lower or upper anvil. There are three different types of HPT, defined as constrained, quasi-constrained and unconstrained, which are dependent upon the precise geometry of the anvils and the degree of restriction on any lateral flow during the processing operation. In unconstrained HPT the anvils are flat and the material flows outwards during processing, whereas in constrained HPT the disk is placed within a cavity in the lower anvil so that any lateral flow is prevented. Most HPT processing is now conducted under quasi-constrained conditions where the disk is contained within depressions on the inner surfaces of the upper and lower anvils so that there is some limited outward flow during the torsional straining [33,34]. The equivalent von Mises...
strain, \( \varepsilon_{eq} \), imposed in HPT is given by a simple relationship of the form [35–37]

\[
\varepsilon_{eq} = \frac{2\pi Nr}{h\sqrt{3}} 
\]

where \( N \) is the number of turns of torsional straining, \( r \) is the distance measured from the centre of the disk and \( h \) is the initial height (or thickness) of the sample. It follows from Eq. (3) that the strain varies across the disk with a maximum value at the outer edge and a value of zero at the center of the disk where \( r = 0 \). Although this suggests the production of gross inhomogeneities when processing by HPT, it has been shown experimentally [32,38–43], and confirmed using strain gradient plasticity modeling [44], that there is a gradual evolution with torsional straining into a reasonably homogeneous microstructure.

**Nature of the microstructures produced by SPD processing**

The introduction of the two processing techniques of ECAP and HPT has led to a major interest in using these techniques and evaluating the properties of the UFG microstructures. Many results are now available showing the applications of these procedures to a wide range of metals and it is convenient to consider examples for both processing methods.

Fig. 3 shows representative results obtained using orientation imaging microscopy and electron backscatter diffraction on high purity Al in (a) the unprocessed condition and (b)–(g) after processing by ECAP through increasing numbers of passes; the unit triangle denotes the crystallographic orientations [45].

**FIGURE 3**

Microstructures in high purity Al in (a) the unprocessed condition and (b)–(g) after processing by ECAP through increasing numbers of passes; the unit triangle denotes the crystallographic orientations [45].
purity (99.99%) aluminium after processing by ECAP for up to a maximum of 12 passes [45]. These samples were processed at room temperature using an ECAP die with a channel angle of $\varphi = 90^\circ$ and an arc of curvature of $\Psi = 20^\circ$. The billets were processed using processing route $B_C$, in which the billets are rotated about their longitudinal axes by $90^\circ$ in the same direction between each pass [46,47]. In Fig. 3, the grain colors denote the orientations of the individual grains as depicted in the unit triangle, different colors in neighboring grains denote misorientations of at least $2^\circ$, black lines denote low-angle boundaries where the misorientations are between $2^\circ$ and $15^\circ$ and red lines denote high-angle boundaries where the misorientations are $>15^\circ$. The initial grain size before ECAP was $\sim1$ mm in Fig. 3(a) and the subsequent illustrations show the microstructures after 1, 2, 3, 4, 8 and 12 passes. After the first pass in Fig. 3(b) there is an array of elongated subgrains but thereafter the microstructure gradually evolves into arrays of reasonably equiaxed grains separated by boundaries having high-angles of misorientation. Measurements showed the average grain size was $\sim1.2$ $\mu$m after 12 passes and the fraction of high-angle boundaries was $\sim74\%$. This measured grain size matches other reports of the grain sizes attained in high purity aluminium after processing by ECAP [48–51].

An example for HPT is shown in Fig. 4 where a Cu–0.1% Zr alloy was processed at room temperature under a pressure of 6.0 GPa through 1 turn in the left column and 5 turns in the right column: the upper row shows the microstructures at the centers of the disks and the lower row shows the microstructures at the edges of the disks [42]. Again, the colors in Fig. 4 correspond to the different orientations of the grains as represented in the unit triangle. It is apparent in Fig. 4(a) that there is an inhomogeneous microstructure after processing through one turn with average grain sizes measured as $\sim580$ nm in the central region and $\sim410$ nm near the edge. After five turns the microstructure is more equiaxed and the grain size is $\sim500$ nm in the center and $\sim410$ nm at the edge. This suggests the microstructure remains reasonably constant at the edge but there is continuous grain refinement in the central region. Ultimately, it is anticipated that the grain size will become reasonably saturated throughout the disk [52,53].

The general principles of grain refinement in ECAP are depicted schematically in Fig. 5 where the grains are shown on the $Y$ plane corresponding to a longitudinal section cut vertically through the ECAP billet [54]. The three rows correspond to the appearance of the grains after pressing through 1, 2 and 4 passes, respectively, and the three columns correspond to processing routes $A$, $B_C$ and $C$: processing route $B_C$ was defined earlier, route $A$ denotes no rotation of the sample between consecutive passes and route $C$ denotes a rotation of $180^\circ$ between each pass [46,47]. The four
The principles of grain refinement in ECAP for 1, 2 and 4 passes using processing routes A, B, C and C: the value of $\eta$ denotes the total angular range of slip for each processing condition [54].

A convenient procedure for evaluating the degree of homogeneity attained in materials after SPD processing is to track the evolution of hardness with additional straining. An example is shown in Fig. 6 where microhardness measurements are recorded on the cross-sectional X planes of a Cu–0.1% Zr alloy processed by ECAP at room temperature (RT) using route $B_C$ with a die having a channel angle of $\Phi = 110^\circ$ through 1, 2, 4 and 8 passes [57]. The colors in Fig. 6 correspond to values of the Vickers microhardness, $H_v$, from 100 to 160 as shown in the color key on the right and the Y and Z axes represent directions perpendicular to the Y and Z planes with the points $(Y, Z) = (0,0)$ corresponding to the centers of the billets on the X plane. It is apparent from Fig. 6 that the microhardness values increase over the X plane with increasing numbers of ECAP passes and ultimately the values saturate in a homogeneous condition of $H_v = 140$ after 8 passes. Close inspection shows there is an initial inhomogeneity in the vicinity of the lower area of the billet after a single pass in Fig. 6(a) but this region of lower hardness is reduced to a width of ~1 mm after 2 passes in Fig. 6(b), it is further reduced after 4 passes in Fig. 6(c) and it disappears after 8 passes in Fig. 6(d). The initial development of lower hardness values near the bottom surfaces of the disks in the early stages of straining is consistent with earlier reports for pure Al [58] and an Al-6061 alloy [59]. Although hardness measurements are generally recorded on the X plane after processing by ECAP, some results are also available showing measurements recorded on the Y or longitudinal planes [57,60,61].

A similar approach may be used for disks processed by HPT and an example is shown in Fig. 7 for a commercial purity (99.5%) Al-1050 alloy using a pressure of 6.0 GPa at room temperature, a...
rotational speed of 1 rpm and with disks processed through totals, \( N \), of 1/4, 1 and 5 turns: again the colors correspond to the hardness values depicted in the color key on the right [40]. As shown in Fig. 7(a), the hardness values are much higher at the edge of the disk after processing through 1/4 turn and there is an extensive region of lower hardness in the central region of the disk. This region of lower hardness is reduced after 1 turn but after 5 turns the hardness values become essentially homogeneous with \( H_v \approx 65 \) over the total area of the disk. Similar results showing lower hardness values in the centers of the disks have been reported also for several materials [32, 41, 43, 62, 63] but there are also reports for high purity Al showing initially higher hardness values in the centers of the disks [38, 39, 64] and for the Zn-22% Al eutectoid alloy where there is an initial higher hardness at the center but the overall hardness values are low because of a reduction during processing in the distribution of Zn precipitates within the Al-rich grains [65]. The hardness values in Fig. 7 are taken on the cross-sectional planes of the disks but there are also some recent reports documenting hardness measurements on vertical sections [66–70].

**Properties after SPD processing**

As anticipated, the grain refinement introduced by SPD processing produces UFG materials having high strength. An example is shown in Fig. 8 where the 0.2% proof stress is plotted against the equivalent strain introduced by ECAP for a number of different commercial aluminium alloys when pressing at room temperature using route B\(_C\); since the processing used an ECAP die with a channel angle of \( \Phi = 90^\circ \), this is equivalent to plotting against the number of ECAP passes where an equivalent strain of zero corresponds to the initial annealed condition [71]. For all alloys, the 0.2% proof stress increases sharply in the first pass but thereafter there is only a minor additional increase up to a maximum of 8 passes.

A second important property is the ability to achieve superplastic properties when testing in tension at elevated temperatures. These properties can be achieved only when the grain size
remains ultrafine at the high temperatures which are needed for diffusion-controlled superplastic flow. Nevertheless, there is now a very large number of reports of superplastic elongations, corresponding to tensile elongations of at least 400% [72], in numerous alloys processed by ECAP [73]. Thus, this property provides an opportunity for using these UFG materials for superplastic forming operations [74]. An excellent example of superplasticity is shown in Fig. 9 where a ZK60 magnesium alloys (Mg–5.5% Zn–0.5% Zr) was processed by extrusion and then ECAP at 473 K for 2 passes using a die with $\Phi = 90^\circ$ and processing route $B_C$ [75]. Following ECAP, a specimen was pulled in tension at 473 K using an initial strain rate of $1.0 \times 10^{-4}$ s$^{-1}$ and the resultant elongation of 3050% represents the highest elongation recorded to date in any magnesium-based alloy processed under any conditions. High tensile elongations have been achieved also when processing by HPT [76,77].

**Future developments in SPD processing**

The preceding discussion confirms the potential for using SPD processing to introduce significant grain refinement into coarse-grained materials, to achieve arrays of equiaxed grains having sizes within the submicrometer range and separated by boundaries having high angles of misorientation and to attain reasonable levels of homogeneity using either the ECAP or HPT processing techniques. A comprehensive review is available which describes the basic characteristics of this type of processing [78].

The commercialization of these materials is now attracting much attention and, as noted in a recent report, the innovation potential for these materials is high [79]. The innovation probability is shown schematically in Fig. 10 as a function of the specific strength of the material [79,80]. This diagram demonstrates that these UFG materials will probably find major applications under extreme environmental conditions and where the required properties are unusually severe. Examples include biomedical applications, their use in aeronautical systems and for high-performance sports applications and for innovative developments in the energy, oil and gas sectors. Processing by ECAP is currently used for the fabrication of Al and Cu sputtering targets in memory components [81] and it has been shown that the ECAP processing technique represents a viable approach for the
40 years ago for the continuous extrusion-forming of metal wires use of the Conform process which was developed in the U.K. about two parallel channels [88]. An alternative approach is to make billet but this may be avoided by using a special ECAP die containing ECAP due to the production of gross distortions at either end of the process such as cold rolling [93] and significant improvement in strength by combining SPD processing with subsequent forming ability for the continuous production of long rods and wires within the die for the conventional Conform process, it is feasible [98, 99].

As discussed in a recent review [86], significant attention is also now being focussed on the further development and improvement of these SPD processing methods. For example, the labor-intensive repetitive pressing of a single billet through a conventional ECAP die can be improved by using a multi-pass ECAP facility [87]. Similarly, there is a considerable material wastage in conventional ECAP due to the production of gross distortions at either end of the billet but this may be avoided by using a special ECAP die containing two parallel channels [88]. An alternative approach is to make use of the Conform process which was developed in the U.K. about 40 years ago for the continuous extrusion-forming of metal wires [89, 90]. By inserting an abrupt abutment into the exit channel within the die for the conventional Conform process, it is feasible to develop an ECAP-Conform procedure which provides the capability for the continuous production of long rods and wires [91, 92]. For biomedical applications with commercial purity titanium, there is evidence for significant improvement in the tensile strength by combining SPD processing with subsequent forming processes such as cold rolling [93] and significant improvement in the wear resistance by depositing a coating on the surface of the processed material [94]. It is possible also to extend the processing operation in ECAP to include the pressing of plate samples [95]. Recent extensions in HPT processing include the use of small cylindrical bulk samples [76, 96, 97] and the development of a continuous processing technique for use with rods and wires [98, 99].

**Concluding remarks**

The processing of ultrafine-grained metals through the use of SPD processing has now reached a critical stage. Sufficient laboratory results are available to demonstrate the general feasibility of this approach and it is recognized that these materials have a high innovation potential. Accordingly, it is reasonable to anticipate significant new developments in this field and new applications for these UFG materials.

**Acknowledgement**

This work was supported by the European Research Council under ERC Grant Agreement No. 267464-SPDMETALS.

**References**


**FIGURE 10**

The innovation potential as a function of material strength showing the use of strong materials in extreme environmental conditions [79, 80].