Bulk nanoSPD materials are materials with nanostructural features, such as nanograins, nanoclusters, or nanotwins, produced by severe plastic deformation (SPD) techniques. Such nanostructured materials are fully dense and contamination free and in many cases they have superior mechanical and functional properties. Here, we provide a critical overview of such materials, with a focus on the fundamentals for the observed extraordinary properties. We discuss the unique nanostructures that lead to the superior properties, the underlying deformation mechanisms, the critical issues that remain to be investigated, future research directions, and the application potential of such materials.

Keywords: Severe Plastic Deformation, Ultrafine-grained Materials, Nanostructures, Properties

1. Introduction In recent years there has been growing interest in bulk nanostructured materials produced by severe plastic deformation (SPD) processing, as demonstrated by the increasing number of publications with high citations [1] as well as numerous specialized conferences, workshops and symposia on the subject (www.nanospd.org).

The critical feature of SPD, in which heavy straining is applied under high pressure with accumulated strains $\varepsilon$ in excess of $\sim 4-6$, makes it possible to produce ultrafine grains (UFG) with sizes smaller than 1,000 nm. Processing by SPD may also lead to a dissolution of second phases, precipitation, amorphization, and other processes producing various nanostructural features such as deformation twins, non-equilibrium grain boundaries, dislocation substructures, solute segregation, and clusters. These changes in the inner make-up of the material may affect the deformation mechanisms and, consequently, change the material properties in a fundamental way. As a result, new structural and functional metals and alloys having superior and unique properties have been developed by SPD processing. [4,7–10]

Over the last decade there has been extensive research into the mechanical and functional properties of bulk nanostructured materials as well as their origin and relationship to fundamental physics. This report gives a critical overview of this research with special attention directed to the extraordinary properties that are enabled by SPD. Our views on the prospects for future developments in the area of nanoSPD materials are also outlined.
2. Grain Boundaries and Other Crystal Lattice Defects Generated by SPD

Grain boundaries in nanostructured materials affect their properties in very significant ways and quite often the UFG metals are referred to as ‘interface-controlled materials’. Different types of grain boundaries are formed by SPD processing and they may be classified as [2,7]

- Low- vs. high-angle boundaries;
- Special vs. random boundaries;
- Equilibrium vs. non-equilibrium boundaries with strain-distorted structures.

In addition, SPD may also produce other structural features in alloys, such as second-phase particles, nanotwins, and solid segregations at the grain boundaries. Such modifications of the make-up of the material at the nano scale can have a strong effect on the material properties. The use of advanced imaging and structural characterization techniques over the past decade has brought about the discovery of three significant nanostructural features of SPD-processed alloys,[8,10–16] which give rise to their remarkable mechanical and functional properties. These are outlined below.

2.1. Nanotwins. A high density of nanotwins produced by SPD was found to increase both the strength and ductility of nanostructured metals and alloys. Figure 1 shows a transmission electron microscopy (TEM) image of UFG Cu after equal-channel angular pressing (ECAP) and cryorolling at the liquid nitrogen temperature; twins 10–20 nm in width are clearly visible.[12] To promote the formation of nanotwins, the following intrinsic material properties and external deformation conditions are required [11]: (1) a relatively low stacking fault energy, (2) a low deformation temperature, and (3) a high strain rate. It should be noted that there is an optimum grain size range conducive for deformation twinning.[11,17–19] This optimum grain size for the formation of deformation twins is affected by both intrinsic properties of the material mentioned above, and it can be estimated using the following equation [11]:

\[
\frac{d_m}{\ln(\sqrt{2}d_m/a)} = \frac{9.69 - \nu}{253.66(1 - \nu)} \frac{Ga^2}{\gamma},
\]

where \( \gamma \) is the stacking fault energy, \( a \) is the lattice parameter, \( \nu \) is Poisson’s ratio, \( G \) is the shear modulus, and \( d_m \) is the optimum grain size.

2.2. Clusters and Segregations. It was found by 3D atom probe tomography that SPD may hinder the formation of precipitates in age-hardenable alloys and instead promote clustering and segregation of alloying elements.[7,15,20–22] For example, the data in Figure 2[23] show that segregations at grain boundaries make-up clusters \( \sim 3–5 \) nm wide in the age-hardenable Al alloy 7075. Moreover, the concentration of alloying elements may be an order of magnitude higher at grain boundaries than in the grain interior.[8,20,22,23]

2.3. Nanosized Particles and Secondary Phase Precipitations. In many alloys subjected to SPD after solid-solution hardening, high densities of nanosized particles appear.[8,10,24] Figure 3 shows an example of nanoparticles that are \( \sim 10–20 \) nm in size in the UFG Al alloy 6061 after ECAP.[24] The presence of

Figure 1. Typical bright-field TEM images of a grain with high density of deformation nanotwins in UFG Cu that was subjected to ECAP and subsequent cryogenic rolling.[12]

Figure 2. Tomographic image of nanostructure of UFG Al alloy 7075. Segregations of alloying elements on grain boundaries and at triple junctions are shown.[22]
Figure 3. UFG structure of Al alloy 6061 after ECAP in parallel channels (four passes): nanosized precipitations in grains are clearly visible in areas A and B at higher magnification.[24]

these nanoparticles is due to dynamic aging and the high density of nucleation sites generated by entangled dislocations. The small size and high density of such particles effectively block and accumulate dislocations not only causing higher strength but also promoting ductility.[13,23–25]

Thus, UFG metals and alloys produced by SPD methods are characterized by a number of nanostructural features which can strongly influence their behavior. In many demonstrated cases, the properties induced by SPD processing are unique to these materials, as will be shown in the following sections.

3. Mechanical Properties of Bulk Nanostructured Materials

Three major properties, namely strength, fatigue behavior and superplasticity, are considered in this section.

3.1. Superior Strength and Ductility. A primary advantage of SPD processing is strength enhancement. Even though the well-known Hall–Petch relation between the yield stress $\sigma_y$ and the grain size $d$,

$$\sigma_y = \sigma_0 + K_{HP}d^{-1/2},$$

may break down for nanomaterials, it commonly holds for UFG materials produced by SPD. Here, $\sigma_0$ and $K_{HP}$ are constants for a given material. Typically, extreme grain refinement by SPD can improve the strength of pure metals or dilute alloys by a factor of 3–8.[26–30] For SPD-processed alloys, grain refinement is often accompanied by phase transformations leading to the formation of nanoclusters, segregations, nanotwins, and dislocation substructures, which provide additional hardening mechanisms. In particular, the formation of grain boundary segregations in the UFG alloys by SPD may suppress the generation of dislocations at grain boundaries and lead to considerable additional hardening.[23]

For example, Figure 4 shows the tensile stress–strain curves of the Al alloys 1570 and 7475. It is seen that the alloys which acquired their UFG structure by high-pressure torsion (HPT) are more than twice as strong as those subjected to conventional hardening.

It was shown[23] that for bulk nanostructured alloys with a grain size of 100–130 nm, the magnitude of $\sigma_y$ is considerably higher than the value calculated from the Hall–Petch relationship. This phenomenon of super-strength of nanostructured alloys was recently demonstrated in various SPD-processed materials, including Al alloys,[24,31] Ti alloys,[8] carbon steels and stainless steels,[32–34] and in an Al–Mg nanocomposite.[35] However, increasing strength of metals and alloys through grain refinement by SPD usually leads to an undesirable drop in their ductility.[8,10,36,37]

The low ductility is caused by the reduction of the strain-hardening capability of a severely deformed material. This can be rationalized in terms of the Considère criterion which states that failure by necking under tensile loading will not occur if the following inequality is fulfilled:

$$\left( \frac{d\sigma^T}{d\varepsilon^T} \right) \geq \sigma^T,$$

where $\sigma^T$ and $\varepsilon^T$ denote the true stress and true strain, respectively. On the other hand, grain refinement enhances the strain rate sensitivity (SRS) of the flow stress and this helps preventing necking.[38] Therefore,
Figure 4. Engineering stress–strain curves of the UFG alloys Al 1570 (a) and Al 7475 (b) processed by HPT in comparison with standard treatment.[23]

3.2. Fatigue Behavior. Fatigue resistance is important for many applications of UFG materials and there has been extensive research in this area. Recent literature surveys on fatigue properties of SPD-processed materials can be found elsewhere.[9,58,59] Empirically, the fatigue limit of coarse-grained materials is proportional to the ultimate tensile strength (UTS) (Figure 5) [59] which may be used to estimate the fatigue limit. However, the fatigue behavior of SPD-processed metals in general is determined by both strength and ductility. Specifically, high-cycle fatigue (HCF) is controlled by the resistance of the material to crack initiation, while low cycle fatigue (LCF) is governed by crack propagation. The life under LCF is largely controlled by ductility while that under HCF is dictated by the fracture strength. Consequently, when SPD processing raises the tensile strength at the cost of ductility, the HCF life is improved while the LCF life is decreased. Again, there are fortunate exceptions to this disadvantageous juncture. It was found [60,61] that ECAP of dilute Cu–Cr–Zr alloys followed by an aging treatment leads to a remarkable improvement of tensile strength and fatigue strength in the HCF regime without sacrificing ductility and LCF properties. Similarly, extrusion + ECAP processing of the ZK60 Mg alloy was shown to lead to an excellent combination of strength and ductility [62] and also brought an impressive improvement of fatigue properties over the entire range of stress amplitudes tested (see Figure 6).[63]

SPD processing also produces good fatigue performance in other metals and alloys. For example, it was reported [64] that an ECAP-processed stainless steel had a record-high fatigue limit due to profuse deformation twinning induced by severe straining. Another example is SPD-processed commercial purity titanium that showed record values of fatigue strength (which were close to or in excess of those for the conventional alloy Ti-6Al-4V).[65–67] These results make it promising to replace this potentially toxic alloy with pure Ti in biomedical applications (see Section 4.8).
3.3. **Superplasticity.** Superplasticity refers to the ability of a polycrystalline specimen to pull out to a very high strain, defined typically as an elongation of at least 400%,\[68\] when tested in tension. The development of a superplastic capability in polycrystalline materials is significant because of the increasing importance of the superplastic-forming industry in the manufacture of complex parts having curved surfaces.\[69\] Superplasticity requires a small grain size, typically below $\sim 10 \, \mu m$, and it is now recognized that the dominant flow process is grain boundary sliding in which the strain rate varies inversely with the grain size raised to a power of 2.\[70\] This means in practice that the extremely small grain sizes produced by SPD processing provide a possibility for achieving superplastic flow at exceptionally rapid strain rates. This was first demonstrated in early experiments on two commercial aluminum-based alloys where elongations of up to 1,000% were attained at strain rates of $10^{-2} \, s^{-1}$.\[71\] This result suggests that an SPD material should exhibit a rapid superplastic-forming capability directly after processing and this was demonstrated by using a biaxial gas-pressure-forming facility and blowing a dome in an SPD-processed Al–Mg–Sc alloy in the short period of only 60 s.\[72\] Experiments also confirmed that the superplastic properties were retained when the material was processed by ECAP and then rolled into a sheet.\[73\]

Although it is relatively easy to achieve exceptional grain refinement in face-centered cubic metals, the situation becomes more difficult in hexagonal close-packed metals such as magnesium because of the limited number of available slip systems. To overcome these difficulties, a two-step processing route was developed in which some initial grain refinement is introduced through extrusion prior to processing by ECAP.\[74\] The effect of this procedure is illustrated in Figure 7 where results are shown for a Mg–8% Li alloy tested in tension over a range of strain rates at 473 K in a cast condition, after casting and extrusion and after casting and extrusion followed by processing by ECAP.\[75\] The changes introduced by these different processing routes are dramatic because the alloy is not superplastic in the cast condition, it is only marginally superplastic after casting and extrusion, but in the cast + extrusion + ECAP condition it is possible to achieve high elongations of up to 1,800%. Using this two-step processing route, it is feasible to achieve excellent superplastic elongations in magnesium alloys and an example is shown in Figure 8 where a ZK60 Mg–Zn–Zr alloy was pulled to failure at an elongation of 3,050%.\[76\] In practice, even larger superplastic elongations may be attained in aluminum-based alloys processed by ECAP and there is a recent report of an elongation of 4,100% in an Al–Mg–Sc–Zr alloy when tested at 723 K at a strain rate of $5.2 \times 10^{-2} \, s^{-1}$.\[77\] Finally, it is important to note that, despite the very small cross-sectional areas of the tensile specimens processed by HPT, it is again possible to achieve excellent superplastic properties with an elongation of 1,800% recorded in an HPT-processed Zn–22% Al eutectoid alloy when pulled to failure at 473 K at a strain rate of $1.0 \times 10^{-1} \, s^{-1}$.\[78\]

4. **Functional Properties of BNM** Nanostructuring of metals may also enhance various functional properties or produce new physical and chemical properties, thereby making them attractive for innovative engineering and medical applications. This section reviews the features and nature of the unusual functional properties observed in bulk nanostructured materials.

4.1. **Electrical Conductivity in Ultrafine-grained Materials.** It is well known that Ag, Cu, Au, and Al are metals with high electrical conductivity (111%, 100%, 78%, and 64% International Annealed Copper Standard [IACS], respectively). In addition to high
conductivity, high mechanical strength of these metals is required for certain applications. Strengthening is generally achieved through strain hardening, solid-solution hardening, precipitation hardening and grain refinement. However, these strengthening mechanisms also lead to lower conductivity because of electron scattering by crystal lattice defects. Recent studies reveal new ways of solving this problem by grain refinement.

The evolution of mechanical properties and electrical conductivity with strain was investigated for pure Cu processed by ECAP,[79–82] accumulated roll bonding (ARB),[83–85] and HPT.[82] As summarized in Figure 9, in pure Cu (99.99%) the hardness increases and electrical conductivity decreases with increasing equivalent strain in the early stages of straining and both level off to constant levels (130 Vickers hardness, 88% IACS) at equivalent strains exceeding ~20.[82] However, the electrical conductivity decreased by only ~12% whereas the hardness increased by ~270% at this saturation level. Subsequent annealing improved the electrical conductivity to 97% IACS while the hardness increment was maintained at a higher level of ~160% (80 Vickers hardness) when compared to the annealed state (50 Vickers hardness). A Corson alloy was processed by HPT and achieved a high strength (~1 GPa).[86] Furthermore, subsequent aging increased the strength to ~1.1 GPa and improved the electrical conductivity to an acceptable level of ~30% IACS.

The advantageous effects of HPT processing on the strength and electrical conductivity of Cu–0.7%Cr, Cu–0.9%Hf, and Cu–0.7%Cr–0.9%Hf alloys were demonstrated.[87] It was reported that pure copper exhibits a high strength over 1 GPa and an electrical conductivity as high as 97% IACS.[48] The sample was synthesized using a pulsed electrodeposition technique which produced grain sizes of 100–1,000 nm containing a high density of nanotwins. The significance of nanotwinning is that twin boundaries block dislocation motion but have little effect on the electrical resistivity. Such combinations of properties are yet to be matched by SPD processing but the above examples suggest that this is potentially achievable.

Another requirement for electrical conductors is light weight and this is especially important for applications in motors, robots, and power transmission lines. Aluminum is the lightest among the high conductivity metals. It was reported[88,89] that UFG Al–Mg–Si alloys processed by ECAP and HPT exhibit a good combination of increased mechanical properties and enhanced electrical conductivity. The increased conductivity was due to second-phase precipitation which reduced the solute concentration in the Al matrix. It was proposed that processing at elevated temperatures to induce dynamic aging may be promising for continuous wire production.[90] Taking advantage of the low solubility of Fe in Al (~0.05 wt%) and a fine eutectic structure at ~1.8 wt%Fe, an Al–Fe alloy was processed.
by HPT and subsequent aging which resulted in a high strength of 600 MPa and a high conductivity of > 50% IACS.[91,92]

4.2. Giant Magnetoresistance (GMR) Produced by HPT. When ferromagnetic particles are finely dispersed in a non-magnetic matrix, magnetoresistance (MR) appears with an isotropic feature. This isotropic MR is called GMR if the MR ratio reaches a magnitude of more than a few tens of percent.[93–100] The Cu–Co system is known as a good candidate for GMR as ferromagnetic Co particles with little solubility of Cu coexist in the Cu matrix.[101] A Cu–10wt%Co alloy was processed using HPT to achieve a fine dispersion of ferromagnetic particles and MR was reported at a level ∼ 2.5% at 77 K with an isotropic feature (Figure 10).[102] The appearance of MR was also confirmed in a Cu–22wt%Fe alloy.[103] While the achieved magnitudes of the MR do not qualify as GMR, the results show that HPT is at least potentially promising for creating GMR in alloys.

4.3. Enhanced Hydrogen Storage Performance of SPD-processed Materials.

4.3.1. Mg and Mg Alloys. Since 2004, ECAP has been used to process nanometals for hydrogen storage, particularly Mg and its alloys (ZK60) (Figure 11).[104–106] The advantages of ECAP over ball milling include prevention of oxidation, which can seriously inhibit absorption/desorption of H2, and the low production cost as large volumes of material can be efficiently processed using ECAP. Furthermore, ECAP avoids health hazards common to toxicity-prone nanopowder-based processes.

A critical requirement for energy storage is stability of the storage capacity and the absorption/desorption kinetics over large numbers of cycles. Ball-milled Mg and Mg alloys rarely meet this requirement unless catalysts are added.[107] As seen in Figure 12, ECAP-processed ZK60 shows high stability of both its capacity for hydrogen uptake and the hydrogenation/dehydrogenation kinetics for at least 1,000 cycles.[105] This was also confirmed for HPT-processed ZK60 for at least 100 cycles (Figure 13,[108]). However, not all SPD-processed materials show high stability. There are several reports [109–111] that ARB- or HPT-processed MgH2 powder has good kinetics but low stability and this was confirmed by a recent high-cycle study [108] as shown in Figure 14. After 40 cycles, the capacity of hydrogen loading clearly decreased. Comparing the long-time stability of SPD-processed materials ZK60 and MgH2, it was concluded that the SPD processes in both materials provide nucleation sites for hydride formation which are, however, not stable in the case of SPD-processed pure MgH2. In that material, it is the comparably large volume of the hydride particles which decreases the hydrogen loading capacity as the hydrogen diffusion becomes sluggish compared with the non-hydrogenated substance.[108]

4.3.2. TiFe Alloys. The TiFe intermetallic with B2-type crystal structure is a well-known candidate for stationary hydrogen storage because of its low hydrogenation temperatures, reversible hydrogenation features, high hydrogen storage capacity, and low price. However, its practical application is limited as it requires an activation process before hydrogenation, which includes exposure to hydrogen atmosphere under high pressures at high temperatures. There have been many attempts to overcome this limitation.[112–120] Recent studies have shown that SPD processing is the way to achieve that, as such an activation process is no longer required when the TiFe is pre-processed by
enhanced diffusion of hydrogen that occurs via HPT-induced microcracks and nanograin boundaries. A further study on TiFe also showed that plastic straining is important in these hard intermetallics. Another SPD process, specifically groove rolling of encapsulated billets, was shown to be effective in activating TiFe samples as well.[123]

4.4. Production of Nanograins in Semiconductors and Occurrence of Photoluminescence.

When crystalline Si is subjected to high pressure, allotropic transformations occur from the diamond cubic structure (Si-I) to high-pressure phases with different crystal structures. These include Si-II with the β-Sn structure, Si-III with body-centered cubic structure, and other phases.[124] Because such high-pressure phases are semi-metallic in nature, they are more likely to deform plastically at room temperature under high pressure. An early study[125] and more recent studies[126,127] reported the formation of nanograins in crystalline Si processed by HPT. The mechanism for the nanograin formation is not understood but it is probably associated with enhanced dislocation activity or transformation-induced grain refinement.[2,128,129] It is interesting to note that nanocrystalline Si (nc-Si) exhibits unique optical properties such as visible photoluminescence (PL) because of quantum confinement.[130] It was shown that annealing after HPT gave rise to a reverse transformation of Si-III and Si-XII to Si-I while retaining the nanograin structure (Figure 16).[127] This is reflected in a broad PL peak centered around 600 nm due to the quantum confinement effect in the Si-I nanograins (Figure 17).[127] The application of HPT to Ge and GaAs also produced nanograins[131,132] and a similar PL peak was also observed for GaAs owing to the nanograin formation by HPT processing and subsequent
annealing.[132] It should be noted that nc-Si is commonly produced by ion implantation,[133] electrochemical etching,[134] and chemical vapor deposition,[135] all of which are suitable for low-dimensional nanostructures such as porous Si and Si dots. It is important to emphasize that the nano-grained semiconductors were obtained in bulk form by virtue of HPT. Thus, the HPT processing of semiconductors can be of great interest for potential applications to optoelectronic devices.

4.5. Superconductors in Nanograin Structures.

Superconducting properties such as the critical temperature $T_c$, critical current density $J_c$, and upper critical field $H_{c2}$ may be affected when the sample size is reduced to the superconducting coherence length ($\xi$) due to the quantum-confinement effect.[136–138] Although the size effect on the superconducting transition was studied by fabricating an ultrathin lead film [139] and an aluminum nanowire,[140] a recent report [141] examined the effect of grain size on the superconducting properties of bulk polycrystalline Nb whose grain size was reduced to $\sim 250$ nm using HPT processing.[142] This grain size is equivalent to $\sim 5\xi$ and the effect was appreciable. It was shown that the values of $T_c$, $J_c$, and $H_{c2}$ were increased due to grain refinement by HPT processing (Figure 18). The increase in $J_c$ can be attributed to the enhanced vortex pinning due to crystal lattice defects such as dislocations and grain boundaries. It was also shown that the residual resistivity $\rho_0$ is governed by the amount of strain imposed by the HPT processing.

Superconductivity was also studied for a well-known system used for superconducting magnets, a Nb-47wt%Ti alloy, to examine the effect of HPT processing on $T_c$. [143] It was found that $T_c$ occurred below 9 K, it decreased with increasing shear strain but rose again with annealing. Although the grain size of the material was comparable with the coherence length (about $8\xi$),[144] the trend of $T_c$ with the imposed strain was
opposite to pure Nb [141] and this was attributed to dissolution of Ti in Nb with straining by HPT. The increase in $T_c$ upon annealing was due to Ti decomposition from a supersaturated state after HPT processing. An important conclusion is that the application of the HPT processing to the Nb-47wt%Ti alloy in conjunction with subsequent annealing leads to an increase in tensile strength as well as bending strength while also maintaining $T_c$ above the value obtained after solution treatment (Figure 19).

4.6. Thermoelectrics. In the field of thermoelectrics, so far mainly two groups of materials were considered in the context of SPD processing (for a detailed review, see [145]): (i) Bi–Te alloys for low-temperature applications and (ii) skutterudites for high-temperature applications. The successes of SPD processing can be judged upon the efficiency of processed thermoelectrics in terms of the so-called figure-of-merit:

$$ZT = \frac{S^2T}{\rho\lambda}.$$  \hspace{1cm} (4)

A large ZT-value is reached either via a high thermovoltage represented by the Seebeck coefficient $S$ or by a decrease in electrical resistivity $\rho$ as well as a decrease in the thermal conductivity $\lambda$. The $S$-value can be enhanced by increasing the gradient of the density of states, for example, by limiting the sample dimensions to a few nanometers or even to the atomic scale as in topological semiconductors, like graphene or silicon [146]). As such dimensions are usually not reached in SPD processing, efforts so far have concentrated on the decrease of $\rho$ and $\lambda$. Now the problem arises of controlling these two quantities independently. This problem needs to be tackled individually for the two groups of materials considered.

The low-temperature thermoelectric Bi–Te alloys exhibit a large crystal anisotropy which means that the texture of the SPD-processed materials is even more important for the resultant ZT value than the decrease in grain size leading to a smaller thermal conductivity through additional phonon scattering. There have been several attempts to increase ZT by application of SPD, mainly HPT [147] and ECAP [148]. HPT processing gave rise to an increased power factor $S^2/\rho$ due to a (110) texture contributing to both a low resistivity and a high Seebeck coefficient (Figure 20, [147]). A real increase in ZT by an SPD method was achieved by the ECAP procedure [148] by carefully choosing the ECAP temperature (773 K) and path (Route A where there is a rotation of the billet by 180° after each pass) in order to obtain high carrier mobility (Figure 21), thus minimizing the electrical resistivity and thereby achieving a figure of merit as high as $ZT = 2.3$.

From among high-temperature thermoelectrics, so far skutterudites have been the subject of SPD processing. Ball-milled skutterudite nanopowder was successfully consolidated by means of HPT at a distinctly lower temperature than the conventional hot pressing, thus yielding much smaller grain sizes. [149] It was found that the thermal conductivity was strongly decreased by
HPT-induced lattice defects although cracks and voids were also generated and increased the electrical resistivity far more so that the overall ZT dropped. This problem was addressed by suitably increasing the HPT processing temperature in order to avoid the formation of cracks and voids, thus keeping the increase in resistivity sufficiently low to achieve an overall increase in ZT (Figure 22).\[145,150\] By optimizing the HPT-processing temperature, pressure, and strain, ZT was further increased by a factor of 2–3 (\[145,150\]; Figure 22) compared with the value before HPT. Finally, with ZT = 1.9, a world record for n-type skutterudites was set using this strategy ([151]; Figure 23). Most recently, another world record ZT = 1.45 was also established for p-type skutterudites [152] by means of a similar preparation procedure. It should be mentioned that this procedure does not introduce new phases,[153] unlike in many alloys processed by SPD,[154] and instead there are changes only in the density and arrangement of SPD-induced crystal lattice defects.[153] Among the latter, there clearly were some which increased the electrical resistivity but without decreasing the lattice thermal conductivity. It must be left to further research whether, in the interest of maximizing ZT, it is possible to remove such defects without losing those that significantly reduce $\lambda$.

4.7. SPD-processed Materials in Biomedical Applications. One application where SPD technologies have achieved one of their most significant successes is the area of medical implant materials. The contemporary development of metallic implant materials is driven by the need for improved mechanical performance and biocompatibility. Different paradigms govern this development for permanent and temporary (biodegradable) implants. While materials for permanent implants, such as bone or tooth replacement, obviously need to be as inert as possible, those for temporary implants are required to degrade at a rate commensurate with the rate of tissue healing. Various materials are being explored as candidates for such applications with an aim to improve their properties by SPD processing.[155] The archetypal alloy systems that offer the best performance for these two kinds of applications are arguably those based on titanium and magnesium. Indeed, Ti forms a protective surface layer of titania and is considered to be bio-inert (thus being suitable for permanent implants) whilst Mg is very reactive and biodegradable.

Figure 20. Electrical conductivity (a) and Seebeck coefficient (b) vs. temperature, for p-type Bi$_{0.5}$Sb$_{1.5}$Te$_{3.0}$ after processing by the Vertical Bridgman Method and HPT.[147]

Figure 21. Dependence of carrier mobility $\mu$ on preferred orientation angle $P_{0.2}$, after applying different numbers of passes of Route A ECAP (labeled ‘ECAE’ in the original figure (from [148]).

Figure 22. Increase in ZT in an n-type skutterudite after HPT processing at temperatures 400°C and 500°C. Letters A, B, and C refer to different strains achieved by HPT (from [145]).

Figure 23. Increase in ZT in an n-type skutterudite after HPT processing at temperatures 400°C and 500°C. Letters A, B, and C refer to different strains achieved by HPT (from [145]).
For titanium-based alloys, among which Ti-6Al-4V is currently most used, a great challenge is the real or perceived toxicity of the alloying elements. Commercial purity titanium grades are thus becoming the materials of choice. To compensate for the loss of strength associated with alloying, SPD techniques are employed, such as ECAP and, recently, its continuous modification ECAP-Conform.[66,155–158] In this way, extreme grain refinement, almost down to the nano scale, is attained, and this leads to an enhancement of tensile strength of pure titanium to the levels of the conventional alloy Ti-6Al-4V and higher with UTS > 1,300 MPa.[66,156,158] Similar encouraging results were obtained for the fatigue strength and this makes it possible to improve the design of medical implants with better functionality (Figure 24).[156,158]

Recent reviews compile the results obtained by ECAP, as well as by more involved SPD processing routes.[66,155] It is especially encouraging that biocompatibility of Ti does not suffer from the ultrafine crystallinity.[159] On the contrary, enhanced rates of attachment and proliferation of osteoblast and fibroblast cells, as well as stem cells,[156,157,160] were obtained in a number of in vitro assays. In vivo studies, while not confirming such enhancement, demonstrated that a spectacular improvement of the mechanical performance of ECAP-modified commercial purity Ti was not accompanied by a loss of biocompatibility.[161]

To further improve biocompatibility, it has been attempted (i) to replace Al and especially V with more biocompatible elements and (ii) to make Young’s modulus close to that of bone in order to avoid the so-called ‘stress shielding’.[162] In particular, Ti–Nb alloys have attracted a great deal of interest. Not only do they meet both these requirements, but they also show good biocorrosion properties.[162] However, since a low Young’s modulus is inherently connected with a relatively low strength, some additional strengthening is required if this material is to be used for medical applications as in implants or prostheses. Processing by SPD can improve the strength via grain refinement.[163–168] However, due to the potential of SPD processing to change phase stability as a result of shear combined with hydrostatic pressure, additional phases may form and this may produce undesired changes—mostly increases—of the overall Young’s modulus (see, e.g.[166]) except when a new phase has a low Young’s modulus too.[167] Also, SPD processing of ternary and quaternary alloys obtained by replacing some of the Nb content by other constituents such as Ta, Zr, and Sn may affect the Young’s modulus in a similar way. Nevertheless, if care is taken in choosing the SPD parameters, such as limited pressure and strain, as well as the number and type of alloy constituents, the strength may be increased by 30–120% (Figures 25 and 26,[157,168]). The selection of an SPD method is also important if a good ductility is required for the intended application. Hydro-Extrusion (HE) may be the SPD method of choice, thereby sacrificing some strength for higher ductility. It is important to emphasize that with all different SPD methods applied to date (Rolling and Folding (R & F), HE, and HPT [168]),
a low Young's modulus was maintained (Figure 26). Smaller changes may happen according to the texture evolution which, again, is specific to the particular SPD method chosen ([168]; Figure 26). While with HPT processing the evolving texture is weak, this is not so for the R & F technique, the Young’s modulus becoming even lower than initially, so that the elastic behavior of the material is closer to that of bone.

Magnesium is very promising for medical applications because of its light weight and bioresorbability. [169,170] As the lightest of all structural metals (except beryllium), the use of magnesium can reduce the weight of many medical structures from wheelchairs and stretchers to surgical tools, to vascular stents and orthopedic implants.[171,172] Magnesium is also among the most biocompatible of metals.

The prospect of nanostructuring magnesium and its alloys to achieve novel properties was recognized more than 20 years ago.[2,173,174] Grain refinement has been regarded as one of the most attractive methods to enhance the performance of magnesium alloys.[175] In addition to grain refinement, substantial texture effects are induced in hcp magnesium alloys by SPD processing. The latter are sometimes sufficiently large to introduce significant mechanical anisotropy, and they are large enough in magnitude to cause net softening upon ECAP [176,177] which is to be avoided through appropriate process design.

Nanostructuring of magnesium alloys offers several advantages and alternatives for biomedical applications, for example in vascular stents. First, reducing the grain size alters the corrosion rate. An AZ31 alloy was processed by ECAP and it was found that the corrosion rate in Hank’s solution was reduced, although not sufficiently to make it suitable for stent applications.[178] An AZ80 alloy was deformed by ECAP and extrusion to obtain an UFG structure that enhanced the electrochemical properties.[179] The polarization layers produced remained stable and completely resisted degradation for up to 96 h. More recently, the electrochemical characteristics of AE21 and AE42 alloys were evaluated after processing by ECAP for eight passes.[180] It was found that the smaller grain size resulting from ECAP enhanced the corrosion rate in AE21 due to increased chemical activity at the grain boundaries whereas, by contrast, the corrosion rate in AE42 was reduced after the same ECAP treatment. In the latter case, the larger effect of increased uniformity of the spatial distribution of alloying elements offsets the effect of a smaller grain size. Clearly, the effects of nanostructuring are complex and alloy dependent and accordingly they must be carefully evaluated for any prospective magnesium alloy.

In particular, osteoconductive characteristics of nanostructured surfaces need further exploration. The in vivo characteristics of both conventional and nanostructured magnesium alloys need to be researched to
The results of numerous studies reported in this article demonstrate clearly that various superior properties, both mechanical and functional, can be obtained in bulk nanostructured materials produced by SPD. The results of numerous studies reported in this article demonstrate clearly that various superior properties, both mechanical and functional, can be obtained in bulk nanostructured materials by SPD. The basic mechanical properties considered include superior strength, enhanced fatigue endurance, and superplasticity. These studies generate a great deal of interest with regard to scientific foundations of the phenomena involved and their practical applications in new structural materials. Recent discoveries have also demonstrated new opportunities for SPD processing with respect to improving functional properties of materials. These include increased electrical conductivity in metals and alloys, giant magnetoresistance, enhanced hydrogen storage performance, occurrence of photoluminescence in nanograined semiconductors, superior thermoelectric properties, and many other unique phenomena that are of immediate interest for various functional applications.

Observations performed during the last decade with a suite of modern techniques including TEM/HREM, X-ray diffraction, 3D-atom probe, and others reveal that not only can SPD processing form UFGs but it can also be used to engineer grain boundary structure and generate nanoparticles, segregations or nanoclusters and other structural elements at nano scale. The type and morphology of such nanostructured elements, as well as their number density, determine new deformation and transport mechanisms responsible for improvement of mechanical, chemical and physical properties of bulk nanostructured materials through SPD techniques.

Over the last few years, studies of bulk nanostructured materials tend to be oriented more toward the development of their advanced and superior properties and in this context the concept of nanostructural design plays an important role. In addition to grain refinement down to the nanometer range, grain boundary structure engineering is also important because boundaries having different structures can exhibit specific transport mechanisms, in terms of deformation and diffusion, and this can be used to control the properties.[7,187] This opens up the potential for developing new ways for improving the properties of ultrafine-grained materials.

5. Summary

As noted earlier, the ability of Mg to be resorbed in bodily fluids makes it a good candidate for biodegradable implants. Various Mg alloys have been tested with respect to their biodegradability. Mg–Zn–Ca alloys have proven to exhibit two advantages at the same time, a good biodegradability and high strength.[181] However, recent experiments with these alloys show that, with respect to the time necessary for tissue healing, these alloys may either degrade too quickly and/or the concomitant hydrogen evolution is faster than the organism can absorb. It was found that the lower the alloying element and/or impurity content of the Mg-alloy, the longer it takes for the alloy to degrade.[182] On the other hand, this means that the potential of the alloy for high strength becomes smaller because second-phase particles cannot form and also solid-solution hardening becomes insignificant. It also becomes harder to reduce the grain size of the Mg alloy below 1 μm with the presence of fewer second-phase particles and/or atoms in solid solution. Very recently, it was reported that strengthening of Mg and its dilute alloys can be affected by the agglomeration of surplus vacancies in vacancy clusters or loops.[183] Figure 27 presents this strengthening effect for the case of biodegradable alloy Mg0.2Zn0.5Ca, which was HPT processed to generate vacancies [184,185] and annealed at homologous temperatures up to about 0.5 $T_m$ (where $T_m$ is the melting temperature in Kelvin) in order to induce agglomeration of these vacancies. Depending on the HPT strain applied, the strength increment amounted to almost 60% of the strength of the as-extruded material (Figure 27). By comparison, grain size strengthening yielded a strength increment of only 19% and this is irrespective of the HPT strain applied (Figure 27,[183]). The hypothesis that vacancies are responsible for the observed strengthening effect is supported by two facts, namely that (i) very similar hardening effects with respect to extent and annealing treatment have been reported for quenched-in vacancies [186] and (ii) careful checks by Atom Probe Tomography [183] ruled out the formation of a second phase as an alternative cause for strengthening.

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2. Observations performed during the last decade with a suite of modern techniques including TEM/HREM, X-ray diffraction, 3D-atom probe, and others reveal that not only can SPD processing form UFGs but it can also be used to engineer grain boundary structure and generate nanoparticles, segregations or nanoclusters and other structural elements at nano scale. The type and morphology of such nanostructured elements, as well as their number density, determine new deformation and transport mechanisms responsible for improvement of mechanical, chemical and physical properties of bulk nanostructured materials through SPD techniques.

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The concept of the nanostructural design of materials is schematically illustrated in Figure 28 [5] using a pictorial representation which modifies and further develops the well-known concept of the contemporary creation of novel materials through the integration of theory and modeling, structure characterization, processing and synthesis, as well as studies of the properties. In comparison with traditional materials design, nanostructuring of bulk materials deals with a far larger number of structural parameters related to the grain size and shape, lattice defects in the grain interior, as well as with rich grain boundary structure, and also with the presence of segregations and second-phase nanoparticles. This provides the possibility to vary the transport mechanisms and change the properties of materials in a desired way. Not only does nanostructuring of bulk materials by SPD processing permits a considerable enhancement of mechanical and physical properties, but it may also be used to create multifunctional materials.[4,8,9,31,188,189] In this respect, it can be anticipated that in the very near future the nanostructuring of materials by SPD processing techniques under different controlled regimes will provide new breakthroughs in the development of materials with superior properties for advanced structural and functional applications.

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