Three-dimensionally gradient harmonic structure design: an integrated approach for high performance structural materials

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ABSTRACT
This paper presents an overview on the peculiar microstructural design, called ‘harmonic structure’ (HS), for improved mechanical performance of structural materials. A well designed powder metallurgy processing approach has been developed to create a unique three-dimensionally gradient HS with controlled bimodal grain size distribution in metals and alloys. The bulk materials with HS exhibited considerably higher strength and improved toughness as compared to coarse-grained structures. The unique HS design promotes uniformity of deformation by avoiding strain localization during plastic deformation. A possible mechanism of deformation behavior of HS has also been proposed based on the available experimental results.

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Microstructural refinement is an efficient method of strengthening metallic structural materials to yield lightweight components with improved performance. In particular, grain refinement in metals and alloys exhibited manifold increments in the strength, wherein materials with submicron-sized ultra-fine-grained (UFG) structure and nano-grained (NG) structure have demonstrated to possess exceptionally high strength values. However, at the same time, the bulk materials with ‘homogeneous’ UFG and NG microstructures exhibited considerably inferior ductility when compared to their coarse-grained (CG) counterparts. As a result, the creation of homogeneous UFG/NG microstructures was not very successful in achieving high strength–high ductility combination, i.e. enhanced toughness, which is an important indicator of improved performance in structural metallic materials. The inferior ductility poses problems not only in subsequent shaping or forming operations but could also lead to catastrophic failure in structural materials.

In recent years, several research efforts were made to achieve a combination of high strength and high ductility through creating heterogeneous microstructures, and it was demonstrated that the metals and alloys with bimodal grain size distribution were extremely promising in delivering high strength together with sufficient ductility. The research efforts on the creation of bimodal microstructures in bulk materials were based on either the conventional ingot metallurgy route consisting of severe plastic deformation (SPD) followed by controlled heat-treatment or the powder metallurgy (PM) based approach based on consolidation of a mixture of severely milled and unmilled powders. The processing approach based on conventional ingot metallurgy approach has an obvious limitation of lack of control over the various important parameters of the
bimodal microstructure, such as grain size, UFG/CG volume fraction, and spatial distribution of UFG and CG areas. As a result, it is difficult to control the large scatter in the mechanical properties. Therefore, such an uncertainty associated with the reproducibility of mechanical properties remains an important issue from reliability of performance viewpoint while considering these bulk materials for the practical applications. The PM-based processing approach consisted of SPD of metallic powders via mechanical milling followed by mixing the mechanically milled powders with un-milled powders in a predetermined volume fraction, and subsequent hot/cold consolidation of the mixture. Such a strategy was very effective in controlling the volume fraction of UFG and CG areas; however, controlling the spatial distribution of UFG or CG areas remained a challenge. To deal with the above-mentioned issues of controlled heterogeneous microstructure, Ameyama et al. proposed an integrated approach to prepare bulk materials with a controlled and unique heterogeneous microstructure, called 'harmonic structure' (HS), with bimodal grain size distribution.[15–25] A schematic diagram illustrating the HS design is shown in Figure 1. The HS is a heterogeneous microstructure with a specific spatial distribution of fine and coarse grains, that is, the CG areas ('core') embedded in the matrix of three-dimensional continuously connected network ('shell') of fine-grained (FG) areas. It would also be worth emphasizing that, in HS, the grain size regime does not change abruptly at an interface, and instead it changes gradually from FG regime to CG regime or vice-versa. Therefore, HS is a unique heterogeneous 'Three-dimensionally (3D) Gradient Microstructure' wherein the FG areas form an interconnected three-dimensional network surrounding CG regions, and CG- and FG areas are periodically arranged in all the directions. In the present paper, an overview on the application of the HS design to various important classes of advanced structural materials is presented. The results illustrating the microstructural evolution at every stage of processing are presented and discussed. Subsequently, the mechanical properties of some of the important harmonic structured metals and alloys are presented and discussed, wherein the processing-structure-properties correlation has been attempted to be made. Finally, an attempt has been made to elaborate the deformation behavior of harmonic structured materials. Therefore, various aspects dealing with the microstructural features, processing methodology, deformation behavior, and mechanical properties of HS design are presented in this paper.

An efficient processing methodology, based on SPD combined with powder metallurgy processing, was developed to prepare bulk materials with such a controlled microstructure. There are two important components to the proposed processing approach: (i) achieving deformed powder particles with bimodal grain size distribution via controlled plastic deformation of powder particles, and (ii) careful consolidation of the deformed powder particles leading to bulk materials with controlled HS. A schematic diagram illustrating the proposed powder metallurgy based processing approach is demonstrated in Figure 2. As depicted in Figure 2, the controlled mechanical milling was carried out primarily by either ball milling (BM) or jet milling (JM) to achieve desired controlled plastic deformation in the metallic powders. The choice of a particular milling process was based on several considerations such as the size of the powder particles, chemical reactivity of the specific material being milled, permissible level of contamination from milling media with respect to specific materials, and ductility and nature of strain hardening behavior of the material being milled. For example, in general, the planetary BM was found to be more effective for achieving controlled SPD in very coarse powder particles (> 200 μm) only, and it was difficult to control the zone of plastic deformation for smaller particles (< 100 μm). Also, the BM had a few other issues related with the ductile and/or reactive metals. These issues include: (i) sticking of the soft metallic powders, such as pure metals as well as some alloys, with the milling balls and vials, (ii) incorporation of surface impurities in the milled powders owing to the use of process control agents, and (iii) some other impurities from the milling media. In order to take care of these issues in specific cases, a relatively cleaner mechanical milling process, called ‘jet milling’, was introduced to achieve controlled SPD in the small-sized softer and/or reactive metallic powders, wherein

![Figure 1. Schematic of the three-dimensional gradient harmonic structure design.](image-url)
Figure 2. Schematic diagram illustrating the proposed powder metallurgy processing to prepare materials with harmonic structure design.

Highly compressed air or gas is used as milling media and interparticle collision under the influence of vortex motion of highly pure inert gases at a very high speed induces SPD at the point of impact in the powder particles. The details of JM apparatus and the mechanism of milling is provided elsewhere.\[22\]

Figure 3 depicts the effect of controlled mechanical milling on the morphology and the microstructure of metallic powders wherein the coarse Ti-6Al-4V alloy powders (particle size > 200 μm) were milled in planetary ball mill and pure Ti powders with relatively smaller particle size (particle size < 100 μm) were milled using

Figure 3. (a) Morphology and cross-section of ball-milled Ti-6Al-4V powder, (b) TEM micrograph of the shell region of the ball-milled Ti-6Al-4V powder, (c) morphology and cross-section of the Jet-milled pure Ti powder, and (d) TEM micrograph of the shell region of the jet-milled pure Ti powder.
It is evident that the overall morphology, that is, spherical shape, of the powder particles did not change significantly as a result of controlled milling (Figure 3(a),(c)). However, it is interesting to note that a featureless ‘shell’ type region is formed near the surface of the powder particles, whereas the original starting microstructure, acicular for Ti-6Al-4V and equiaxed for pure Ti, is retained in the inner parts of the powder particles (Figure 3(a),(c)). A representative Transmission Electron Microscopy (TEM) micrograph and its corresponding selected area diffraction pattern (SADP) of the featureless shell regions of the ball-milled Ti-6Al-4V powders and jet-milled pure Ti powders are shown in Figure 3(b),(d), respectively. The TEM micrographs of the featureless shell regions clearly demonstrate that the severely deformed shell region consists of submicron-sized crystallites. Therefore, the above results clearly show that the controlled mechanical milling induces SPD limited to the near-surface region of the powder particles, whereas the effect of plastic deformation remains extremely small in the inner ‘core’ region. As a result, the powder particles with bimodal grain size distribution are formed, consisting of inner CG ‘core’ region and UFG outer shell region. However, it must be realized that a gradient of degree of deformation exists in the milled powders and the severity of the accumulated plastic strain decreases from the particle’s surface towards the center of the particles.

The above results clearly demonstrate the effectiveness of BM process for the coarse Ti-6Al-4V powders and JM for fine-sized Ti powders in inducing controlled SPD, leading to the bimodal core/shell structure in the metallic powder particles. In particular, the successful application of new JM process to achieve controlled deformation in the small-sized, ductile, and chemically reactive pure Ti powders is of important technological interest. The effectiveness of JM to create controlled severely deformed shell region in the small-sized powders appears to be related to the very small area of contact between the small-sized particles during their mutual collision. As a result, a very limited area and volume undergoes SPD during each impact. Hence, a recurrence of such collisions leads to the formation of limited and severely deformed shell zone. It has also been demonstrated that the shell/core fraction can be successfully controlled by controlling milling time and number of milling passes in BM process and JM process, respectively.[19–22]

The milled bimodal powders are consolidated at elevated temperatures to prepare bulk materials. Recently, spark plasma sintering (SPS) has been used extensively for the consolidation due to rapid sintering together with avoidance of deformation induced texture during consolidation process. Microstructures of the sintered compacts, thus prepared, of different types of metals and alloys, such as pure Ti, Ti-6Al-4V alloy, and SUS304L stainless steel, are presented in Figure 4. Figure 4 shows the microstructure of the sintered compacts prepared from different metals and alloys (a) pure Ti, (b) Ti-6Al-4V alloy, and (c) SUS304L grade stainless steel.
demonstrates the grain size and spatial grain size distribution through color coded grain size distribution map. It can be noted that the sintered compacts consist of a peculiar microstructure wherein the FG areas form an interconnected three-dimensional network surrounding CG microcrystalline regions, which are distributed periodically. Furthermore, it can also be noted that the HS consists of a smooth grain size gradient from shell to core regions, that is, grain size increases continuously from UFG shell region toward the CG core region. This typical microstructure is referred as ‘harmonic structure’. Therefore, harmonic structure design is a specific heterogeneous 3-D Gradient Structure with an interconnected three-dimensional network of FG regions, and periodically arranged CG and FG areas in all the directions. Clearly, the proposed strategy is extremely successful in creating HS in a variety of pure metals and alloys. It would also be worth mention that the FG and CG regions of the HS are derived from the severely deformed ‘shell’ and CG ‘core’ regions, respectively, of the milled powders. Therefore, the volume fraction of the FG region can be precisely controlled by controlling the severely deformed shell region in the milled powders. Moreover, it is envisaged that the grain size of the shell region can also be controlled by optimizing a proper set of sintering temperature and time. Finally, it would be worth emphasizing that a variety of powder consolidation methods, such as Hot Roll Sintering (HRS), Hot Isostatic Pressing (HIP), Hot Forge Sintering (HFS), and Hot Extrusion (HE), can be used to prepare near-full density HSed bulk materials.

Figure 5 demonstrates a comparison of mechanical properties of various metals and alloys with HS and their CG counterparts prepared from initial powders. In Figure 5, normalized yield strength refers to relative yield strength of HS specimens of a metal/alloy with respect to its CG counterpart tested under similar conditions. Similarly, the normalized stress-strain area refers to the relative area under the engineering stress-strain curve of a HS metal/alloy with respect to its CG counterparts. Here, area under the stress-strain curve has been presented as an indicator of toughness of the material. It can be noted that the normalized yield strength of the HS metals and alloys was considerably higher as compared to their conventional homogeneous CG counterparts. Since the area under the stress-strain curve is considered as a representation of the toughness of materials, the HS materials also exhibited improved toughness as compared to their CG counterparts. Therefore, it is apparent that the creation of harmonic structure design leads to improved mechanical properties in most of the metals and alloys, suggesting that the HS metallic material would also exhibit an improved performance in service. At this juncture, it would be worth mentioning that, depending on the specific requirements, a desired combination of strength and ductility can be adjusted by controlling the core/shell volume fraction and grain size, which can be controlled, eventually, through a proper adjustments of milling and sintering conditions.[15–17,19–21]

Since the nature of distribution of fine- and CG areas in the bimodal microstructure could be an important factor in deciding about the final mechanical properties. The effect of topological distribution of fine- and coarse areas on the properties was also evaluated wherein random bimodal was created by mixing severely milled powders with un-milled initial powders.[19,24,25] It was observed that the random bimodal structured specimens demonstrated higher strengths when compared to bulk CG specimens. Moreover, other important observations were also made from these studies: (a) Both random and HS bimodal exhibit same strength but HS exhibit higher ductility when compared to random bimodal; (b) the HS specimens show extremely small variation of properties when compared to random bimodal specimens.[19,24,25] Moreover, in general, it was also observed that the harmonic structure design promotes uniformity of deformation when compared to random bimodal structure, leading to suppressed strain localization and relatively higher tensile ductility.

It is believed that, in random bimodal-grained structure, the FG regions facilitate higher strength, whereas CG regions assist in retaining higher ductility. Since the HS materials have a specific topological distribution of fine- and CG regions, such a typical morphology is bound to have a pronounced effect on the deformation behavior of the harmonic structured materials. Figure 6 shows a simplified schematic diagram illustrating a
possible deformation mechanism to explain the exclusive deformation behavior of the HS bulk materials. In HS design, the relatively stronger FG ‘shell’ can be visualized as three-dimensional interconnected basic structure, that is, skeleton, of the microstructure. Hence, the HS materials cannot be plastically deformed without achieving deformation in the stronger FG skeleton structure. As a result, interconnected FG shell structure becomes the high stress area and dominates the early stages of deformation, leading to higher yield strength. To accommodate the overall shape change in the specimens, the plastic deformation also brings about shape change to the well-arranged periodic CG core regions together with the interconnected FG shell network. However, the strain localization does not occur in the FG areas owing to their inability to accommodate any large extent of strain in the form of dislocations and other defects. Since ductile/soft core areas are constrained by the stronger shell structure, these soft regions also deform in order to accommodate the overall shape change of the shell structure and the deformation occurs in such a way that the continuity of the material is remained intact rather than deforming in purely tensile mode. To achieve this goal, plastic strain is transferred toward the ductile regions through the interface of CG-/FG areas. The plastic deformation of the core also leads to the strain hardening, resulting in the increased strength with increasing straining. It appears that such a complex deformation behavior not only keeps the strength of the HS higher but also delays the point of effective plastic instability when compared to CG structure. Hence, an evolution of a complex strain distribution in the HS during plastic deformation appears to be very effective in sustained work hardening up to large strain values, leading to higher strength values throughout the deformation process.

In summary, an integrated approach based on controlled mechanical milling followed by hot consolidation of powders has been developed, which is extremely effective in the creation high performance bulk structural materials with a three-dimensionally (3D) gradient bimodal microstructure termed as harmonic structure. The versatility and flexibility of the proposed approach lies in the fact that a variety of milling (e.g. BM, JM, etc.) and consolidation techniques (e.g. SPS, HIP, HRS, HFS, and HE etc.) can be used to create bulk materials with HS. The controlled mechanical milling forms a peculiar UFG-Core/CG-Shell structure in the powder particles. The subsequent consolidation of these particles results in bulk materials with a typical and unique ‘3D Gradient Structure’ wherein the FG areas form interconnected three-dimensional network surrounding CG regions, and CG- and FG areas are periodically arranged in all the directions. The pure metals and alloys with HS exhibited considerably higher yield strength, ultimate tensile strength, and apparent toughness when compared to their homogeneous CG counterparts. The initial deformation stages and strength of the HS is governed by the characteristics of the interconnected network of the FG shell regions, such as grain size, width of the shell, presence of other strengthening mechanisms. The uniformity of deformation and overall ductility is governed by the ductile CG core region and its ability to undergo strain hardening up to large strain values. It was also observed that the HS promotes uniformity of deformation by avoiding strain localization during plastic deformation. It has been indicated that the HS leads to very efficient accommodation of plastic deformation via gradual distribution of strain in the CG core areas, leading to very effective sustained work hardening to a large strain values. Therefore, it has been observed that the peculiar characteristics of HS induce a complex deformation behavior in the bulk materials, leading to a combination of high strength and high ductility at the same time.

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