Postprint of Gradient Nanostructured Materials

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Abstract

This paper briefly reviews recent domestic and international research advances in gradient nanostructured materials, including the classification of gradient nanostructures, the main performance characteristics of these materials, and their preparation and processing techniques. Furthermore, some fundamental scientific issues confronting gradient nanostructured materials and explorations into their industrial applications are discussed with an outlook on future developments.

Full Text

Gradient Nanostructured Materials

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Abstract

In this paper, research progresses on gradient nanostructured materials in recent years are briefly reviewed, including classification of gradient nanostructures, properties and processing techniques of gradient nanostructured materials. Perspectives and challenges on scientific understanding and industrial applications of gradient nanostructured materials are addressed.

KEY WORDS nanostructured materials, gradient nanostructure, property, synthesis and processing

Nanostructured materials are defined as materials whose structural unit size (such as grain size in polycrystalline materials) is at the nanometer scale. Their distinctive structural characteristic is the presence of a large number of grain boundaries or other interfaces, which endows them with mechanical and physicochemical properties fundamentally different from conventional coarse-grained materials [1]. Over the past three decades, research has shown that nanostructured materials typically exhibit very high strength and hardness. Without altering chemical composition, structural nanocrystallization can increase strength and hardness by several times or even tens of times compared to coarse-grained counterparts of the same composition, representing a new approach for developing high-strength materials. However, the significant improvement in strength and hardness is accompanied by a marked reduction in plasticity and toughness, loss of work hardening capability, and deteriorated structural stability. These performance drawbacks have constrained the application and development of nanostructured materials [2].

Recent studies indicate that hierarchical architecture of nanostructures can effectively overcome these disadvantages while retaining their advantages, with gradient nanostructure being one important architectural type. Gradient nanostructure refers to a spatial gradient variation of structural unit size (such as grain size or lamellar thickness) from the nanoscale continuously increasing to the macroscale [3]. Alternatively, it can be described as a material where one portion consists of nanostructure and another portion consists of coarse-grained structure, with a continuous gradient transition in structural unit size between these two regions. The essence of gradient nanostructure is a gradient variation of grain boundary (or other interface) density in space, which corresponds to gradient variations in many physical and chemical properties. This gradient change in structural size differs from simple mixing or composite of structures with different characteristic sizes (such as nano-grains, submicron grains, and coarse grains), effectively avoiding performance discontinuities caused by abrupt changes in structural feature size. It enables coordination between structures of different characteristic sizes, allowing simultaneous manifestation of multiple mechanisms corresponding to each feature size, thereby optimizing and improving overall material performance and service behavior.

Many material properties vary with structural unit characteristic size, and these variations become particularly significant when the structural unit size is reduced to the nanometer scale. For example, the strength of metallic materials increases with decreasing grain size, showing exceptionally dramatic enhancement when grain size is reduced to the nanoscale, as illustrated in Figure 1 [Figure 1: see original paper][4]. Compared to gradient microstructures (where size increases from micron to macro scale), gradient nanostructures correspond to a much broader range of strength variation, enabling extensive strength modulation. Moreover, because nanostructured materials possess unique physicochemical properties such as high diffusion rates and chemical reactivity, gradient nanostructures are endowed with entirely new functional characteristics. Consequently, gradient nanostructured materials have become a new research focus in recent years.

1 Classification of Gradient Nanostructures

For materials with identical chemical composition and phase constitution, gradient nanostructures can be categorized into four basic types, as shown in Figure 2 [Figure 2: see original paper][4]:

(1) **Gradient nano-grained structure**: The structural units are equiaxed (or approximately equiaxed) grains with grain size gradient from nano to macro scale (Fig. 2a).

(2) **Gradient nano-twin structure**: Grains contain substructures—twins, with uniform grain size distribution but twin/matrix lamellar thickness gradient from nano to macro scale (Fig. 2b).

(3) **Gradient nano-lamellar structure**: The structural units are two-dimensional lamellar grains with lamellar thickness gradient from nano to macro scale (Fig. 2c).

(4) **Gradient nano-columnar structure**: The structural units are one-dimensional columnar grains with columnar diameter gradient from nano to macro scale (Fig. 2d).

These four basic structure types can have different interface structures, such as high-angle grain boundaries, low-angle grain boundaries, and twin boundaries. Composite gradient nanostructures can be formed by combining two or more of these basic structures. For instance, a composite structure of gradient nano-grained and gradient nano-twin structures exhibits both grain size gradient and twin density gradient, meaning both grain boundary density and twin boundary density vary gradiently.

When chemical composition and phase constitution change, even more complex composite gradient nanostructures can form, such as gradient nano-grained structures with compositional gradients or gradient nanostructures with phase composition gradients (where phase interface density varies gradiently). An example is the gradient nanograined structure composed of martensite and austenite phases formed in 316 stainless steel [5].

Gradient nanostructures can exist in different forms in materials. In most cases, the nanostructured portion is located at the material surface while the coarse-grained structure remains in the interior. This surface gradient nanostructure can fully exploit many excellent properties of nanostructures, substantially improving surface properties and many surface structure-sensitive performance characteristics (as discussed below). Alternatively, the nanostructured portion can be placed in the interior with coarse-grained structure at the surface, which may also exhibit unique properties, though research on this configuration is limited.

2.1 Surface Hardness Gradient and Wear Resistance

According to the classic Hall-Petch relationship, material strength and hardness increase with decreasing grain size D, proportional to $D^{-1}/^{2}$ (as shown in Figure 1 [Figure 1: see original paper][4]). Therefore, gradient variation in grain size corresponds to gradient variation in strength and hardness. If a material has a nano-grained surface layer and a coarse-grained core, its surface hardness can be several times higher than that of the core at the same chemical composition, creating a substantial hardness gradient from surface to interior. For example, in a pure Cu sample with surface gradient nano-grained structure [3], the surface layer grain size is about ten nanometers with hardness reaching 1.65 GPa, while the core coarse-grained structure has hardness of only 0.75 GPa. The hardness varies gradiently within a 500 m thick surface layer. Research shows that twin boundaries in nano-twin structures have strengthening effects similar to conventional grain boundaries, with strength and hardness increasing as twin lamellar thickness decreases within a certain range. At the nanoscale, low-angle grain boundaries show no significant difference in strengthening effect from high-angle grain boundaries. Therefore, other types of gradient nanostructures also produce similar hardness gradients. For instance, Fe-25Mn steel with gradient nano-twin structure [6] shows hardness decreasing gradiently from 5.4 GPa in the surface nano-twin structure to 2.2 GPa in the core coarse-grained structure. In a pure Ni sample with gradient nano-lamellar surface structure [7], the surface nano-lamellar structure (average thickness 20 nm with low-angle grain boundaries between lamellae) exhibits hardness as high as 6.4 GPa, several times that of the core coarse-grained structure (1.5 GPa).

Material wear resistance correlates with hardness. According to the classic Archard wear law, wear resistance is proportional to the hardness of the worn surface. Nanostructured materials, whether bulk, thin film, or coating, often exhibit superior wear resistance compared to coarse-grained materials [8]. The hardness gradient formed by surface gradient nanostructure is highly beneficial for improving wear resistance.

Under dry friction sliding conditions, pure Cu [9], low-carbon steel [10], medium-carbon steel [11], Cr-Si alloy [12], and aluminum alloy [13] samples with surface gradient nano-grained structures prepared by surface mechanical grinding technology show varying degrees of wear resistance improvement. Under low load conditions, wear resistance improves by 3-4 times, though it approaches that of coarse-grained samples as load increases due to the limited thickness of the gradient nano-grained structure layer. Under abrasive wear conditions, Hadfield steel with gradient nano-grained surface structure shows better wear resistance than coarse-grained material when using "soft" abrasives, but deteriorated wear resistance with "hard" abrasives [14]. Under oil lubrication conditions, whether sliding or fretting friction, surface gradient nano-grained structure substantially improves wear resistance. For example, under conditions of 50 m amplitude, 50 N load, and 20 Hz frequency, the wear resistance of pure Cu with gradient nano-grained surface structure increases by nearly 20 times compared to coarse-grained samples [15]. Gradient nano-grained surface structure 304L stainless steel shows 3 times improved wear resistance at 40 N load and 120 r/min rotation speed [16].

It should be noted that the high surface hardness of metallic materials with gradient nano-grained surface structure does not always lead to significant wear resistance improvement. For instance, the formation of gradient nano-grained surface structure does not improve wear resistance for 304L stainless steel under dry friction conditions [16] or for 718 alloy under fretting friction conditions [17], possibly related to the plastic deformation characteristics of gradient nanostructures under specific friction conditions. Ferritic steel (AISI52100) with gradient nano-grained surface structure shows wear resistance comparable to coarse-grained samples under dry friction sliding conditions [18]. After annealing to allow appropriate grain growth, its wear resistance improves by 4-5 times. Analysis indicates that optimal wear resistance corresponds to the best combination of strength and plasticity.

2.2 Strength-Ductility Matching

Strength and ductility/toughness in metallic materials are typically mutually exclusive. High-strength metals often have poor ductility, while metals with good ductility generally have low strength. This strength-ductility "trade-off" relationship has become a critical bottleneck in materials development. Gradient nanostructure provides a new approach to solve this problem.

Surface mechanical grinding treatment (SMGT) was used to prepare a gradient nano-grained structure on the surface of a pure Cu rod, with grain size gradiently increasing from about ten nanometers at the surface to tens of micrometers in the rod core. The thickness of the gradient nanostructure reached hundreds of micrometers. Room-temperature tensile tests [3] showed that the yield strength of the pure Cu rod sample with gradient nano-grained surface structure increased by about one time compared to coarse-grained Cu samples, while maintaining the same tensile ductility, as shown in Figure 3a [Figure 3: see original paper][3]. The surface gradient nanostructure layer is the main reason for the strength improvement. Although the gradient nano-grained layer occupies a small area fraction in the sample cross-section (about 9%), its contribution to strength improvement is substantial due to the very high yield strength of the nano-grained structure (the yield strength of the outermost 50 m-thick nano-grained structure reaches 660 MPa, more than ten times that of coarse-grained structure). Quantitative analysis indicates that the gradient nano-grained layer contributes up to about one-third of the overall sample strength.

The tensile ductility of gradient nanostructures is largely determined by the coarse-grained matrix. The matrix coarse-grained structure possesses good plastic deformation capability, high tensile strain, and strong work hardening capacity during tensile deformation. The gradient structure can effectively suppress strain localization and early necking that may occur in the surface nano-grained structure during deformation, thereby delaying deformation localization and crack initiation in the nano-grained structure and enabling the nano-grained structure to exhibit good tensile plastic deformation capability. Experimental observations show that when the tensile strain of gradient nanostructured pure Cu exceeds 100%, the surface nano-grained layer can still deform compatibly with the coarse-grained matrix without crack formation.

The strength-ductility combination exhibited by pure Cu samples with gradient nano-grained surface structure is fundamentally different from that of plastically deformed coarse-grained samples. As shown in Figure 3b, at the same strength level, the tensile uniform elongation of gradient nanostructured samples is several times that of coarse-grained deformed samples. This excellent combination of high strength and high tensile ductility opens new avenues for developing high-performance engineering structural materials.

The key to breaking this strength-ductility "trade-off" relationship lies in the unique deformation mechanisms of gradient nanostructures. During room-temperature tensile deformation, obvious grain growth occurs in the surface gradient nano-grained layer, which is distinctly different from conventional thermally-driven grain growth and also fundamentally different from traditional deformation mechanisms such as dislocation motion, twinning, grain boundary sliding, or creep. This grain growth process is driven by mechanically-induced grain boundary migration.

During tensile deformation of gradient nano-grained structures, grain size in the surface layer increases with deformation amount. The average grain size in the outermost layer (20 m thick) increases from tens of nanometers to about 400 nm before stabilizing. Grain growth corresponds to decreases in strength and hardness. Therefore, during tensile deformation of gradient nano-grained structures, the core coarse-grained structure gradually hardens with increasing tensile strain, while the surface gradient nanostructure layer gradually softens due to grain growth (Figure 4 [Figure 4: see original paper][19]), leading to reduced hardness gradient between surface and interior. When tensile strain increases to a certain level, the hardness throughout the sample becomes uniform and the hardness gradient disappears [19].

Similar phenomena of improved strength without ductility loss have been observed in other gradient nano-grained structure materials, such as low-carbon steel [20], 316 stainless steel [21], IF steel [22], and TWIP steel [23]. Wu et al. [22] found that during uniaxial tensile deformation of gradient nano-grained structures, the grain size gradient leads to the formation of a strain gradient, which changes the stress state in the gradient nano-grained structure layer. This change in stress state promotes dislocation storage and interaction, resulting in additional work hardening that causes an increase in work hardening rate during tensile deformation and improves material tensile ductility. They pointed out that this additional work hardening behavior is an intrinsic property of gradient grain structures that does not exist in homogeneous structure materials.

Recently, the author [24] analyzed and discussed gradient nanostructures and their mechanical behavior, comparing the strength-ductility synergy of gradient nanomaterials with conventional coarse-grained materials, nanocrystalline materials, and nanocrystalline-coarse-grained mixed materials, as shown in Figure 5 [Figure 5: see original paper][24].

2.3 Fatigue Properties

Refining grain size to the nanometer scale in polycrystalline materials can substantially increase strength and hardness, but does not guarantee improved fatigue resistance. Experimental results show that ultrafine-grained pure Cu samples (with submicron grain size) exhibit poorer strain-controlled low-cycle fatigue performance but better stress-controlled high-cycle fatigue performance compared to coarse-grained samples. For nanocrystalline pure Ni samples, crack propagation resistance in stress-controlled fatigue experiments is significantly lower than that of ultrafine-grained samples, indicating that fatigue resistance deteriorates markedly when grain size is refined to the nanoscale.

Under cyclic loading, fatigue cracks typically initiate at sample surfaces. If the surface layer structure is refined to nanoscale while the core retains coarse-grained structure, with grain size varying gradiently from surface to interior, the surface nano-grained structure can effectively prevent fatigue crack initiation due to its high strength, while the core coarse-grained structure can hinder crack propagation due to its high plasticity. The combined action of these two mechanisms can simultaneously resist both fatigue crack initiation and propagation. Therefore, surface gradient nanostructure can substantially improve material fatigue resistance. This inference has been confirmed by experimental results.

Roland et al. [25] prepared a gradient nano-grained structure layer about 40 m thick on the surface of 316L stainless steel rod samples with 6 mm diameter, with the outermost layer having an average grain size of about 20 nm. Test results showed that fatigue strength improved in both low-cycle and high-cycle fatigue experiments. The fatigue limit increased from 300 MPa for coarse-grained samples to 400 MPa, representing a remarkable 33% improvement. Analysis indicated that the fatigue limit improvement originated from the surface gradient nanostructure rather than residual stresses in the samples. The thickness of the gradient nanostructure layer significantly affects the degree of fatigue performance improvement. Recently, using SMGT, a gradient nanostructure layer about 200 m thick was prepared on 316L stainless steel rod samples with 6 mm diameter. Tensile-tensile fatigue test results showed that the fatigue limit increased by nearly 80% compared to coarse-grained samples. If the same thickness surface gradient nanostructure was prepared on 3 mm diameter samples, the fatigue limit improvement could reach as high as 130%. This demonstrates that the thicker the gradient nanostructure layer relative to the sample, the more significant the fatigue performance improvement. In pure Cu samples with surface gradient nano-grained structure, the fatigue limit increased by about 75%

compared to uniform coarse-grained material, and fatigue life improved by one order of magnitude.

Gradient nanostructures can also effectively improve fatigue performance in engineering alloys. After preparing a gradient nanostructure layer on a commonly used martensitic stainless steel (Z5CND-16), its torsional fatigue performance was substantially enhanced [26]. When a 150 m thick gradient nano-grained structure and deformed structure were formed on the surface of 6 mm diameter coarse-grained samples, the fatigue strength increased by 46% (Figure 6 [Figure 6: see original paper][26]). The gradient nano-grained structure is the main reason for the fatigue strength improvement. In the original samples, about 16% residual δ-ferrite existed, and fatigue cracks often initiated near δ/M interfaces. Surface nanocrystallization homogenized the microstructure, substantially refined the δ-ferrite, and made its distribution more uniform, thereby effectively suppressing fatigue crack initiation.

2.4 Surface Alloying

Due to the presence of numerous grain boundaries, triple junctions, and other structural defects, nanocrystalline materials provide fast diffusion channels for atoms and additional driving force for chemical reactions (higher interface excess energy). The high density of grain boundaries also provides nucleation sites for chemical reactions. Consequently, atomic diffusion rates and chemical reactivity in nanocrystalline materials are significantly higher than in conventional coarse-grained materials. Utilizing this characteristic of nanostructures, preparing gradient nanostructures on metal surfaces can substantially accelerate surface alloying kinetics, reduce alloying temperatures, shorten processing times, and expand the industrial application range of surface alloying.

Surface mechanical attrition treatment (SMAT) was used to prepare a gradient nano-grained structure on pure Fe samples. Secondary ion mass spectrometry measurements of Cr diffusion behavior in the gradient nanocrystalline structure revealed that the diffusion coefficient of Cr in nanocrystalline Fe at 300-380 °C is 7-9 orders of magnitude higher than the bulk diffusion coefficient in Fe and 4-5 orders of magnitude higher than the grain boundary diffusion coefficient in coarse-grained Fe [27]. Radioactive isotope tracer method was used to measure the diffusion behavior of 63Ni in the gradient nano-grained surface structure of pure Cu samples [28], as shown in Figure 7 [Figure 7: see original paper][28]. The nominal diffusion coefficient at the outermost nano-grained structure (within 10 m thickness) was more than two orders of magnitude higher than the diffusion coefficient along conventional high-angle grain boundaries in coarse-grained Cu samples. The significantly enhanced diffusion rate in gradient nano-grained structures originates from the high density of grain boundaries and triple junctions, as well as numerous dislocations and other defects generated by deformation.

Reactive diffusion is also substantially enhanced in gradient nanostructures.

Test results of Zn diffusion behavior in the gradient nanostructure surface layer of pure Fe [29] showed that the growth rate of Fe-Zn compound layers in the gradient nanostructure surface layer at 280-340 °C was significantly higher than that in coarse-grained Fe substrates. The growth activation energy was 108.0 kJ/mol, substantially lower than that of Fe-Zn compound layers in coarse-grained Fe (167.1 kJ/mol), and the reaction initiation temperature was about 21 °C lower than in coarse-grained Fe. The high density of grain boundaries in gradient nanostructure surface layers increases the thermodynamic driving force for compound formation and provides numerous preferential nucleation sites. The high density of nucleation sites results in newly formed reaction products with smaller grain sizes, i.e., higher interface density, which in turn accelerates solute atom transport and enhances the growth kinetics of reaction products.

Conventional gas nitriding of steel materials is generally performed above 500 °C for several to tens of hours due to the low diffusion rate of N atoms in Fe lattice and the formed nitrides. Gradient nanostructures can significantly accelerate gas nitriding kinetics, enabling gas nitriding of steel at lower temperatures.

As shown in Figure 8 [Figure 8: see original paper][30], pure Fe samples with gradient nanostructure surface layers successfully achieved surface nitriding after gas nitriding at 300 °C for 9 h, obtaining a nitride layer about 10 m thick (composed of e-Fe2~3N and γ-Fe4N nanocrystals) and a transition layer about 30 m thick beneath it, where numerous e-Fe2~3N phases formed on ferrite grain boundaries [30]. Under the same nitriding conditions, no nitrides formed in coarse-grained pure Fe samples (Figure 8a).

Chromizing experiments on low-carbon steel [31] and H13 steel [32] with gradient nanostructure surface layers show that at lower temperatures, gradient nanostructures can significantly increase Cr diffusion rate and compound formation capability in the sample surface layer. At higher temperatures, the promoting effect of gradient nanostructures on chromizing gradually decreases due to grain boundary recovery and grain growth. Utilizing the compound phases formed at lower temperatures and their thermal stability, a low-temperature and high-temperature two-step composite chromizing process was developed: solid powder composite chromizing treatment at 600 °C for 120 min followed by 860 °C for 90 min. This produced a continuous chromizing layer about 20 m thick on low-carbon steel with gradient nanostructure surface layer, five times thicker than that on coarse-grained samples under the same treatment conditions. Compared to coarse-grained samples, the chromizing phase in gradient nanostructure surface layers has finer grain size, higher (Cr, Fe)23C6 phase content, and more uniform microstructure distribution, resulting in significantly improved corrosion resistance in acidic media containing SO4^{2-} or Cl^{-} and 3-6 times improved wear resistance.

Gradient nanostructure surface layers can accelerate surface alloying processes for other engineering metallic materials, including chromizing of H13 hot work die steel [32], nitriding of 304 stainless steel [33] and 38CrMoAl steel [34], and aluminizing of low-carbon steel [35], P92 ferritic/martensitic steel [36], and

AZ91D magnesium alloy [37]. Preparing surface gradient nanostructures can reduce surface alloying treatment temperatures and shorten processing times, not only broadening the application range of conventional surface alloying but also creating conditions for developing new surface alloying systems.

2.5 Surface Deformation Roughness

Due to crystallographic orientation differences between grains, conventional coarse-grained materials often develop deformation inhomogeneity between grains during plastic deformation (such as tension, bending, or drawing), leading to surface roughening and increased roughness, commonly known as the "orange peel" effect. This surface roughening often creates stress concentration or becomes crack initiation sites during subsequent deformation, affecting the deep processing performance of metallic materials.

If a material surface has gradient nanostructure, the nano-grained structure can effectively suppress deformation inhomogeneity, thereby avoiding the "orange peel"effect. Experimental results [3] show that for pure Cu samples with gradient nano-grained surface structure, surface roughness remained at 0.3 m before and after tensile deformation to fracture (with 58% elongation), with no "orange peel" effect observed. In contrast, coarse-grained samples with the same initial surface roughness developed obvious "orange peel" effect under the same tensile elongation, with surface relief reaching several micrometers.

Using SMGT technology, a gradient nano-grained structure was prepared on one side of a 750 m thick pure Cu sample while the other side remained coarse-grained. After electrochemical polishing, both sides achieved nanometer-scale roughness. During uniaxial static tensile deformation, surface morphology observation (Figure 9 [Figure 9: see original paper][4]) revealed obvious intergranular deformation inhomogeneity on the coarse-grained side, which gradually developed into larger relief with microcracks forming between some grains. On the gradient nanostructure side, the surface maintained good uniformity after deformation with surface roughness below 100 nm and no crack formation [3]. This demonstrates that gradient nanostructure surface layers possess superior plastic deformation capability and deformation uniformity compared to coarse-grained structures, effectively suppressing "orange peel" effect during metal processing and improving surface deformation roughness and deep processing performance.

2.6 Other Properties

Grain size nanocrystallization and increased grain boundary volume fraction lead to corrosion behavior in nanostructured metallic materials different from conventional coarse-grained materials. The corrosion behavior of metallic materials with surface gradient nano-grained structures shows two scenarios: Under non-passivating conditions where stable dense passive films cannot form, surface gradient nano-grained structure in 316L stainless steel exhibits poorer pitting resistance in Cl^{-}-containing solutions [38]. In most cases, however, surface gradient nano-grained structures in passive metallic materials more readily form protective passive films, resulting in significantly better corrosion resistance than coarse-grained materials. For example, Ni-22Cr-13Mo-4W-3Fe alloy in Cl^--containing acidic solution [39] shows improved corrosion resistance due to changes in passive film semiconductor type caused by gradient nanostructure surface layers. Ti-6Al-4V alloy in Ringer’ s solution not only forms passive oxide films [40] but also enables spontaneous film growth in Ringer’ s solution, substantially improving implant biocompatibility. It should be noted that the preparation and processing techniques of gradient nanostructures affect grain size, layer depth, and sample surface roughness, thereby influencing corrosion resistance.

Gradient nanostructure surface layers can improve bonding between dissimilar materials and enhance adhesion between hard films and metals. For example, surface gradient nanocrystallization treatment improves bonding strength between 304 stainless steel and hard films (CrN, TiN, DLC, etc.) and enhances film wear resistance [41,42]. The improved film-substrate bonding mainly originates from rapid diffusion of elements from the film or transition layer into the gradient nanostructure layer, facilitating metallurgical bonding formation.

3 Preparation and Processing of Gradient Nanostructured Materials

Currently, gradient nanomaterials are typically prepared through gradient plastic deformation and gradient physical or chemical deposition methods.

3.1 Gradient Plastic Deformation

Plastic deformation can generate numerous defects (such as dislocations, grain boundaries, twin boundaries, etc.) in metals. By controlling plastic deformation conditions, grain structures can be refined to submicron or even nanoscale. The principle of grain refinement is that deformation causes massive dislocation multiplication, and dislocation interactions produce numerous subgrain boundaries and grain boundaries that gradually subdivide original coarse grains into fine grains. When grain refinement reaches a certain level, dislocation generation balances with dislocation annihilation due to structure recovery, and grain size stabilizes. The steady-state grain size depends on material type and composition; generally, the steady-state grain size of pure metals is at the submicron level, while that of alloys can be reduced to the nanoscale. For metallic materials with low stacking fault energy, numerous twins can form under appropriate deformation conditions. Twin boundaries “cut” original coarse grains into nanoscale-thick lamellar structures, and further deformation fragments these nano-lamellae to form randomly oriented nanograins.

Research shows that the grain refinement process induced by plastic deformation is controlled by strain amount, strain rate, deformation temperature, and deformation gradient, and is also related to material properties. Larger strain produces smaller grains, but grain size saturates when strain reaches a certain critical value (i.e., steady-state grain size). Higher strain rate or lower temperature is more favorable for grain refinement. Increased deformation gradient tends to reduce grain size.

Based on understanding of grain refinement by plastic deformation, several surface plastic deformation techniques have been developed in recent years to achieve grain refinement in material surface layers. Since strain amount, strain rate, and deformation gradient vary gradiently from surface to interior, gradient nanostructures are formed in material surface layers. Surface gradient deformation modes can be divided into three categories, as shown in Figure 10 [Figure 10: see original paper][4]:

(1) **Surface impact gradient deformation** (Fig. 10a): Hard indenters or shot peening media repeatedly impact the material surface multiple times, generating repeated plastic deformation in the surface layer. Strain and strain rate decrease gradiently with increasing depth, while cumulative strain increases with impact number. An example is surface mechanical attrition technology [43,44].

(2) **Surface grinding gradient deformation** (Fig. 10b): A hard spherical indenter is pressed into the material surface and moved relative to the material, using friction between indenter and material to cause plastic deformation in the surface layer. Strain and strain rate decrease gradiently with increasing depth, while cumulative strain increases with grinding passes and pre-indentation depth. An example is surface mechanical grinding technology [45].

(3) **Surface rolling gradient deformation** (Fig. 10c): A hard spherical indenter is pressed into the material surface and rolled on the material surface, using rolling to generate plastic deformation in the surface layer. Strain and strain rate decrease gradiently with increasing depth, while cumulative strain increases with rolling passes and pre-indentation depth.

All three deformation modes can achieve gradient plastic deformation in surface layers, producing gradient nano-grained and gradient nano-twin structures. The surface gradient nanostructure layer thickness (structure with grain size at nano and submicron scales) can reach hundreds of micrometers, and the deformation layer depth can reach millimeters.

Gradient plastic deformation can also be realized in bulk materials. Wei et al. [23] torsionally deformed bulk TWIP steel samples, where the core experienced small deformation while the edge experienced large deformation, creating a deformation gradient in the sample and obtaining gradient nano-twin structure.

3.2 Gradient Physical or Chemical Deposition

During physical deposition (such as sputtering deposition, laser or electron beam deposition) and chemical deposition (CVD, electrochemical deposition) of materials, the microstructure of deposited materials is determined by deposition process kinetics. By controlling the kinetics of physical or chemical deposition processes, the structure and composition of deposited materials can be effectively controlled to achieve gradient variations in structure or composition. For example, using electrochemical deposition and controlling deposition rate and other conditions, pure Ni samples with grain size gradient from 10 nm to tens of micrometers can be prepared, with both sample thickness and grain size gradient being adjustable [46].

Phase transformation is another important approach for structure refinement. By controlling phase transformation conditions (such as temperature, pressure, etc.) to adjust the kinetics of phase transformation nucleation and growth, the microstructure of transformation products can be tailored. Therefore, if phase transformation temperature or pressure can be made to distribute gradiently in a sample, enabling gradient control of phase transformation kinetics in the material, gradient nanostructures can be obtained.

4 Applications and Prospects

The series of characteristics exhibited by gradient nanostructures (Figure 11 [Figure 11: see original paper][4]) create new opportunities for developing new materials and processing technologies. Utilizing these characteristics can substantially improve the comprehensive performance of materials, not only expanding the application range of existing materials but also enabling performance improvement of low-cost materials through subsequent gradient nanocrystallization treatment to meet or even exceed the performance of high-cost materials. For example, the comprehensive performance of ordinary carbon steel can be brought up to alloy steel standards through treatment, reducing material costs. Similarly, gradient nanocrystallization treatment technology can be combined with other low-cost material processing technologies to replace high-cost processing technologies and achieve cost reduction.

The high wear resistance of gradient nanostructures has already found industrial application. Baosteel Research Institute used ultrasonic mechanical grinding surface nanocrystallization technology to treat cold rolling leveling rolls (made of bearing steel), obtaining a gradient nanostructure surface layer (with nanograined structure layer thickness of about 10 m). This substantially improved roll wear resistance without changing the material composition, increasing service life from the original 2-3 days to 6-9 days and doubling the roll change interval. Currently, surface gradient nanocrystallization treatment technology for rolls has been put into mass production at Baosteel.

The excellent properties of gradient nanostructures can be achieved through localized treatment of materials or components to selectively improve performance, thereby enhancing overall material or component performance and lifespan. For example, welded joints are often the "weak link" where component fracture failure occurs. Gradient nanocrystallization treatment of welded joints can improve the solidification microstructure and its uniformity, increasing strength and deformation capability. Shaft diameter transition zones in shaft components are typically locations prone to fatigue fracture, largely limiting component service life. Surface gradient nanocrystallization treatment of shaft diameter transition zones can improve their fatigue resistance, thereby enhancing the overall service life of shaft components.

One of the important future challenges in this research direction is developing preparation and processing technologies for gradient nanostructures to meet broader and deeper industrial application requirements. Further expanding the gradient variation range of nanostructures and achieving precise control of gradient nanostructures are the main challenges facing preparation and processing technologies. Efficient, convenient, and low-cost preparation and processing technologies are crucial for promoting the application and development of gradient nanostructured materials. Correspondingly, deeper understanding of gradient nanostructure-property relationships also facilitates further development of preparation and processing technologies.

Many fundamental scientific issues in gradient nanostructured materials research remain to be solved, including the intrinsic relationships between gradient nanostructures and mechanical, physical, and chemical properties; gradient control and its influence on various properties; characteristics of plastic deformation mechanisms at different hierarchical levels in gradient nanostructures and their differences from corresponding homogeneous structure deformation mechanisms; interaction and transfer mechanisms between deformation mechanisms at different hierarchical levels in gradient nanostructures; and thermal, mechanical, and chemical stability of gradient nanostructures and their control laws. Solving these fundamental issues depends on in-depth systematic experimental research combined with theoretical and computational simulation studies, also posing new challenges for interdisciplinary integration of materials science with related disciplines such as mechanics, condensed matter physics, and chemistry.

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