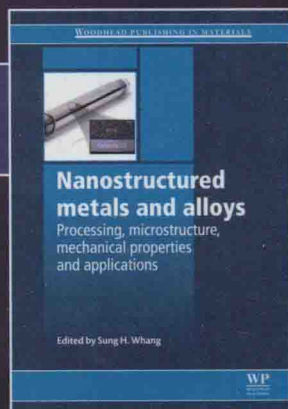


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Nanostructured Metals and Alloys:
Processing, Microstructure,
Mechanical Properties and Applications

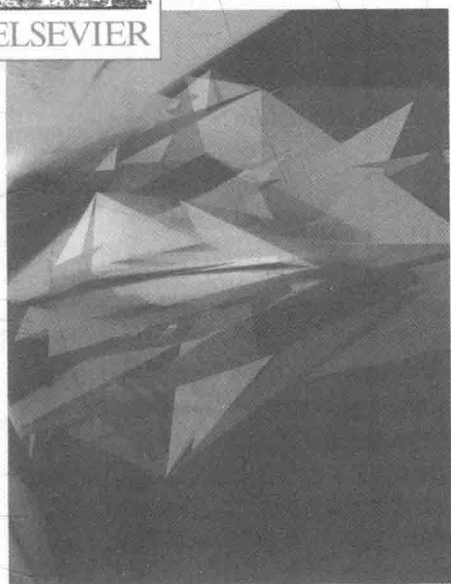
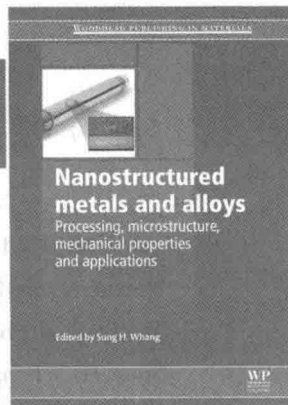
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Introduction

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Recent nanotechnology for material applications deals with a very wide range of material groups and various aspects of materials problems. Since the volume of the accumulated knowledge and database for the subjects stemming from worldwide research and development has been rapidly escalating, this book intends to limit its coverage to the recent progress on nanostructured metallic materials for structural applications.

Since 'nanostructured materials' were first defined by Gleiter,^{1,2} research and development in the fields of nanostructured materials have flourished over the last two decades. Currently nanostructured materials are conveniently defined as materials made of a microstructure less than 100 nm in length in at least one dimension whereas ultrafine-grained materials (UFG) possess a grain size range between 200 nm and less than 1 μm in diameter. But, for practical reasons, nanostructured metallic materials that have been prepared for research and development contain a wide range of grain size distribution from tens of nanometers to a submicrometer. For example, research on optimizing the mechanical properties of nanostructured materials requires manipulation of its bimodal and multimodal grain size distribution. In this case, the grain size ranges from nano size (NG) to submicron size (UFG). Therefore, for practical structural applications, it is envisioned that nanostructured bulk metallic materials may contain both nanoscale as well as submicron-scale microstructures in the future. This book deals with metallic materials that have various grain size distributions: nanoscale grains or nanomicrostructure other than nanograins or submicron scale grains or submicron microstructure other than submicron grains or a combination of all these.

The history of metallic materials shows that an appetite for higher strength/specific strength, and better ductility and toughness for structural applications has been the main driving force for research and development for better and even better materials in the last century, as well as this century. Recent nanostructurizing approaches to the metallic material systems continue this effort. To achieve this desire, scientists and engineers always look into smaller-scale worlds from micron- to submicron-, and submicron- to nano-dimensions for their solutions. Long before such recent endeavors became a fashion among materials scientists and engineers, it was recognized that nanoscale microstructure has great potential for changing the landscape in advanced engineering materials and manufacturing. For example, new high-strength aluminum alloys were produced for the first time utilizing the nanoscale Guinier-Preston zone³ and ultrafine-layered wire with extremely high strength⁴ long before the current nanotechnology debut. The

discovery of the Hall–Petch relationship also suggested that new high-strength materials might be fabricated with materials with nanoscale grain sizes.

In the last two decades, research and development into nanostructured metallic materials have been largely focused on metallic materials with two different microstructures: nanograined structures and embedded nanomicrostructures other than nanograins; and also the effort has been largely devoted to four different subject areas: processing and fabrication, characterization of material properties, microstructural characterization, and engineering design and development for new products and applications.

The first hurdle to overcome in this effort has been the large-scale processing of high quality of nanomaterial for use in research and development. Of course, many technically challenging problems emerge in the course of processing of such nanomaterials. In general, the bulk forms prepared by different processes contain different structural defects and impurities. As a result, the mechanical properties of the specimens of an alloy prepared by different processing routes exhibit substantial deviation, particularly in structure-sensitive properties such as deformation behavior, ductility, fatigue, superplasticity and creep. This deviation poses serious problems for scientists in the analysis and interpretation of the experimental results and in arriving at meaningful conclusions. In addition, many of the processes face other challenging engineering problems that require each process to demonstrate the feasibility of scaling-up for industrial applications.

As the nanomaterials research fields continue to expand and the accumulation of knowledge from the research escalates, it becomes clear that it is increasingly difficult to cover the progress made in these fields adequately in a single publication. Thus, the focus of the current book is placed on the recent progress on nanostructured metallic materials in bulk forms, in their processing, microstructure, mechanical properties and structural applications. For those who are interested in these subjects and want to know the depth and breath of the issues, there are references available for additional reading, which have reviewed and summarized the progress made in these areas in the past.^{5–7} This brief introduction on the subject areas is given for readers who come from other fields.

Processing

It is imperative to provide nanostructured metallic materials of sufficient quality and quantity for research and development in order to realize the envisioned progress in this field. There have been many processing approaches available for producing a small quantity of nanostructured metals based on ‘top-down’, and ‘bottom-up’ approaches¹ in three different phase forms – vapor, liquid or solid – utilizing all available technological means. The bottom-up approach includes inert gas condensation, chemical vapor condensation, pulse electron deposition,

etc. Nevertheless, the structural application requires a substantial quantity of nanostructured materials in three dimensions, which eliminates the majority of possible bottom-up processing approaches as candidates for the current effort, at least at this stage. Currently, that leaves only a handful of potentially viable processes for research and development in bulk nanostructured metallic materials. For these reasons, this book includes only those processing methods that could be serious candidates for producing nanostructured metallic materials in the near future.

This book introduces several promising processing approaches for nanostructured metallic materials, which include 1) solid deformation processing: equal channel angular pressing (ECAP), high pressure torsion (HPT), accumulative roll-bonding (ARB), mechanical attrition (MA) and mechanical machining process (MM); 2) solid reaction processing: ultrafine bainite or pearlite structure in carbon steels using a combination of deformation and thermal reaction; and 3) liquid–solid transformation: involving a transformation from liquid to solid phases, e.g. from the molten phase to metallic glass and subsequently to crystallization; electrodeposition processing; and thermal spray processing, from molten droplets to solidified droplets containing nanograins.

Severe plastic deformation processes

Historically, a large plastic deformation and the resulting microstructural refinement in metals and alloys have been investigated by a number of researchers.^{8–11} Nevertheless, the concept of relating severe plastic deformation (SPD) to ultrafine microstructure as well as unique properties has been put to test by Valiev and co-workers in the 1980s and thereafter,^{12–14} which has contributed to the popularization of current SPD technology for nanostructured metallic materials. Both high pressure torsion (HPT) pressing and equal channel angular pressing (ECAP)¹¹ use the same principle: that hydrostatic pressure permits a very large shear deformation in ductile metals, at a strain as high as strain of 4–5, which translates into the dislocation density up to $10^{14–17} \text{ mm}^{-2}$.^{15,16} Repeating the process cycle in SPD results in ultrafine grains (100–300 nm). On the other hand, although the ARB process as another form of SPD generates fine-grained microstructure by a large accumulative deformation similar to ECAP, the approach is substantially different in that in ARB processing,^{17,18} a very large accumulative deformation is applied to a thin sheet by a series of repetitive fold-and-roll processes without hydrostatic pressure where the surfaces of sheets in the folded sides convert to grain boundaries by cold welding. In the processing, the ultrafine grain refinement occurs by the introduction of new grains in the old grains during dynamic recovery and post annealing. Both ARB and ECAP deformation generate new grains of high angle grain boundaries, and the fraction of such boundaries increases with an increasing number of cycles. ARB is particularly advantageous for producing a sheet form of nanostructured metallic material.

There are many roadblocks in the way of ECAP and HPT becoming industrially viable processes. They include the inability to produce the desired dimensions – length, width and thickness of continuous bulk forms – at this stage. Nevertheless, in one area, the wire processing by a large accumulative deformation is successful in producing the required dimensions. For example, a fine wire of Mn steel is made by drawing 10 mm diameter rods of a dual-phase microstructure of martensite and ferrite and of the composition of Fe-0.2C-0.8Si-1Mn (wt-%) into individual strands of 8 μ m diameter wire. This wire drawing amounts to a huge deformation of a true strain in excess of 9. The dislocation cell size in the deformed wires is found to be 10–15 nm.^{19,20}

Another form of SPD is mechanical attrition, which is basically high impact ball-milling, and produces very large plastic deformation. Although an initial development aimed to produce new alloys by mechanical alloying,²¹ the same technique can be employed to produce microstructural refinement. In the process, metallic powders undergo fracture and plastic deformation in which the powders can form mechanical alloying or generate nanoscale microstructures such as fine grains or fine precipitates. The deformed nanograins in this process exhibit deformation shear bands²² like any other highly deformed nanograins produced by other processing techniques. Nevertheless, these nanostructured powders are not a final product, but a precursor material. The nanopowders may be consolidated into nanostructured bulk materials or they can be sprayed for nanostructured coatings.

Consolidating powders into a bulk material is a challenging process because of pores or oxides or other potential contamination introduced into the matrix, some of which are produced during milling and consolidation; and second, these precursor powders undergo microstructural coarsening or grain growth during thermal consolidation. A recent approach using a cryogenic atmosphere in mechanical attrition shows clear improvement in effective milling and a reduction in contamination.²³ SPD metals with UFG can be produced by a conventional machining process, whose microstructural refinement mechanisms have been known for some time. The grain size produced in machining depends on processing parameters, but it can be as low as 200 nm. Besides, the machining can produce bulk forms of UFG products such as foils, sheets, or rods, directly from the coarse-grained bulk metals.²⁴ The challenging aspect of this approach is to control the microstructure via machining parameters such as strain, strain rate and temperature throughout the entire operation. Alternatively, individual UFG chips produced can be consolidated into a bulk form by various consolidation techniques, which are still in the early stage of development.

Solid reaction processes

Nanomicrostructures other than nanograin structures can be generated and produced in a controlled manner by thermal reaction and diffusion. One recent interesting approach is to examine the possibility of creating nanostructure in

conventional high-strength steel material, which is difficult to process using conventional SPD approaches due to its high flow stresses.

In the past, bainite steels have been in use for a long time, and the nucleation and kinetics of bainite formation have also long been understood. In another recent approach, the bainite reaction can be made to produce nanoscale bainitic ferrite plates (20–40 nm) by heat-treating bainite steel at relatively low temperatures for a longer duration. This is only possible in steels with a relatively high concentration of carbon. For example, in Fe-0.78-0.98 C-Si-Mn-Cr-Mo alloys, an enhanced nucleation of ferrite in austenite after supercooling is possible at the low temperatures (125–325°C) for one to six days' holding time during which grain growth is suppressed.^{25,26} This type of steel containing nanostructures exhibits an extremely high strength comparable with that of maraging steels. The advantage of bainite steels over martensitic steels is that martensite steel has limited dimensionality due to the fact that it needs a high cooling rate to produce martensite, while nanoscale bainite steels can be produced in larger dimensions due to their flexible heat treatment requirements and no requirement of high cooling. High-silicon bainite steels also exhibit a combination of high strength and toughness.²⁶

Liquid–solid transformation processes

Liquid–solid transformation processes have two different approaches. First, a molten alloy is solidified into an amorphous phase, from which nanocrystalline precipitates or nanograins can be produced by controlled heat treatment for crystallization.²⁷ The amorphous matrix turns into partially or fully nanocrystalline matrix depending on heat treatment conditions. The maximum dimensions of a bulk amorphous metal, however, are limited due to the fact that 1) a critical cooling rate is required for amorphous formation and 2) each alloy has its own glass forming ability. The second process includes thermal spray coating, in which the feed material is melted and broken into fine droplets before solidifying on the substrate surface. In this process, the stability of the molten phase is important during melting and flight.²⁸ The feedstock could be powders or solid wires. A general rule of thumb is that any material that has a stable molten phase and can be processed into the appropriate feed specifications, can be thermal sprayed. The heat source used to heat and accelerate the feedstock is generated either chemically via oxygen–fuel combustion or electrically via an arc.

Mechanical properties

One of the most pronounced mechanical properties of nanostructured metals is their extraordinary high yield strength compared to those of conventional coarse-grained metallic materials. But, the downside of this material is its well-known poor ductility. Earlier efforts to test the strengthening behavior of nanometals with respect to grain size led to the discovery of a breakdown of the Hall–Petch (H–P)

relationship.^{29,30} This unexpected behavior was identified as the ‘inverse H–P relationship’. Since then, this unexpected softening behavior of nanostructured metals has been a subject of intensive research and the center of discussion. Furthermore, not only is strain hardening (the result of characteristic dislocation pile-ups in coarse-grained metals) absent in nanostructured metals with grain size less than approximately 20 nm, but also any dislocation pile-up in nanograins has not been observed using high-resolution microscopy. Thus, in nanograined metals, grain boundary (GB) deformation has to be the main mechanism for plastic deformation, considering the fact that 1) nanograins become an inactive component in deformation, and 2) the volume fraction of grain boundary and triple junction under the single-digit grain size matrix could be anywhere from 10% to as much as 30%. For these reasons, the focus of research moved from grain deformation to grain boundary deformation for nanograined metals. For the last two decades, unique deformation mechanisms of nanostructured metals and alloys based on grain boundary deformation mechanisms have been investigated, in which each of different deformation modes such as tensile deformation, superplastic deformation, creep and fatigue failure has been studied separately to capture a complete picture of the deformation mechanisms. Research results on these subjects are presented and discussed throughout various chapters in Parts II and III of this book..

Strength and ductility

The Hall–Petch relationship tells us that we could achieve strength in materials that is as high as their own theoretical strength by reducing grain size. Indeed, their strength continues to increase with decreasing grain size to approximately 20–30 nm where the strength peaks. Indeed, the peak yield strength of pure nanostructured copper with grain size approaching approximately 20 nm can reach as high as 800–900 MPa^{29,31–33} compared to 200 MPa for coarse-grained copper. But decreasing grain size beyond 20 nm reverses the H–P effect: in other words the material starts to soften instead of further strengthening. In general, nanostructured metals are characterized as having very high strength with poor ductility. In other words, the strength increase trades off with ductility in nanostructured metallic materials.

As an exception, artifact-free nanocrystalline copper with a grain size of 30–60 nm was found to possess a very high yield strength, and good ductility such as a fracture strain of 0.06 to 0.12 (Eng).^{34,35} Such relatively ductile behavior of nano-copper may be explained by a number of models: dislocations stored in larger grains, grain boundary sliding, Coble creep (GB diffusion), localized shear microbands, twinning, etc.

For nanostructured metals with a wide distribution of grain size, none of the above models can be excluded. But, when the grain size distribution is narrow and its median value is close to 20 nm or less, only grain boundary deformation modes, i.e. grain boundary sliding, grain boundary rotation or Coble creep must

be considered since the grains are regarded as plastically non-deformable islands that are embedded in the network of grain boundaries. For nanostructured metals, it may be possible that all these GB deformation models are operating in an optimized manner.³⁶ Another important factor is the effect of impurities on GB deformation. For example, nano-copper with contaminants does not exhibit such ductile behavior, probably due to the fact that the impurity has a negative influence on GB deformation, which is a subject of future investigation.

Deformation mechanisms

In the past, tensile testing of nanostructured metallic materials has been performed with various grain sizes from the ultrafine scale to the nanoscale, as small as 10 nm in diameter. In addition, the samples prepared by different processing routes have contained different levels of atomic as well as macro defects. Thus, one must be careful in analysing and interpreting the experimental results from such diversified material sources. In fact, this has been a challenging aspect for investigating deformation mechanisms of nanostructured metals in the past.

In general, the tensile deformation of nanostructured metals shows that the flow stress starts to decline right after yielding, indicating an absence of strain hardening behavior. This is an indicative of the fact that the dislocation pile-up doesn't occur beyond the yield point in nanostructured metals. To explain this behavior, it is proposed that the number of dislocations in the pile-up continues to decline with decreasing grain size.^{37,38} Thus, there must be a critical grain size where a single Frank–Read source can operate in a grain. Near such a critical grain size, the dislocation pile-up would no longer occur due to the very high shear stress required for the generation of any additional dislocation, and consequently, the Hall–Petch relationship cannot be established. This would explain why the H–P relationship breaks down in nanostructured metals.

For these reasons, dislocation pile-up mechanisms would no longer be useful for nanostructured metals with a grain size less than 20–30 nm. Thus, the focus has been shifted to grain boundary deformation in recent years. The fact that the volume percentage of grain boundary and triple junction significantly increases and reaches as much as 30% for a grain size less 10 nm makes GB deformation more significant. But the details of GB deformation in nanostructured metals are very complex. Furthermore, direct observation of deformation defect structures using high-resolution microscopy is scarce.

Therefore, research into GB deformation mechanisms has largely taken two tracks: 1) developing theoretical approaches that are based on classical deformation models for superplasticity; 2) performing computer simulations based on molecular dynamics under various stress and temperature conditions. The theoretical approach is considered to test the predetermined framework against experimental measurements whereas MD simulations let atoms and groups of atoms play the game without knowing the outcome.

From this prospect, MD simulations could provide insightful information about the process and mechanisms of plastic deformation. Since, in nanograined metals, tensile deformation, superplastic deformation and creep have a common thread, i.e. grain boundary deformation, it may be possible to develop a unified model that can describe these three deformation modes in the future.

GB deformation models

Although the three different deformation modes – time-independent deformation, superplasticity and creep—are connected through grain boundary deformation mechanisms, conceptually it can be said that each of the modes is made of different levels of contributions by stress-induced GB deformation and thermally-induced GB deformation. In general, it is understood that grain boundary sliding in nanostructured metals occurs by GB dislocations if dislocations are available under applied shear stress, and by thermally activated local shear events, which occur by uncorrelated individual atomic jumps and the movement of small groups of atoms.

In particular, nanostructured metals are made of grains whose boundaries are not only nanoscale, but also in the non-equilibrium state (majority). Thus, thermally induced GB deformation becomes important in this type of materials.

With such a conceptual background, Conrad *et al.*³⁹ proposed that the macroscopic shear occurs due to thermally activated atomic shear in the nano-grain boundary, i.e. GB sliding. Fu *et al.*, following the idea of a neighbor-grain-exchange mechanism in superplastic deformation by Raj *et al.*,⁴⁰ introduced a plastic accommodation term to the thermal shear stress in Core–Mantle nano-grains.⁴¹ The results show that the strain rate in nano-copper with grain size less than 10 nm at 300K could reach a significant level indicating that GB sliding would be real possibility under diffusional sliding with plastic accommodation. In recent years, Wang *et al.*⁴² suggested that grain rotation and grain coalescence in the direction of shear would be possible during plastic deformation. Ovid'ko demonstrated that such a rotation of grains could be indeed possible by creating disclinations during such a rotation.⁴³ Furthermore, Murayama *et al.*⁴⁴ reported that TEM images from a milled Fe sample showed a partial disclination dipole. Another deformation structure reported was shear band formation as a localized deformation mode in ultrafine-grained iron.⁴⁵

Another important issue is non-equilibrium GB,⁴⁶ which is a center of dislocation sink and generation. The fraction of non-equilibrium boundary increases with decreasing grain size. It is important to understand the role of the non-equilibrium GB in deformation. For example, 1) the emission of partial dislocations from triple junctions and non-equilibrium GB as part of the accommodation mechanisms to local shear events would trigger the formation of stacking faults and twins in nanograins, and 2) non-equilibrium GB acts as a dislocation sink and may assist dynamic recovery during deformation. Despite the