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NANOSTRUCTURED MATERIALS-PROCESSING, STRUCTURES, PROPERTIES AND APPLICATIONS

Structural nanocrystalline materials: an overview

Carl C. Koch

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Abstract This paper presents a brief overview of the field of structural nanocrystalline materials. These are materials in either bulk, coating, or thin film form whose function is for structural applications. The major processing methods for production of bulk nanocrystalline materials are reviewed. These methods include inert gas condensation, chemical reaction methods, electrodeposition, mechanical attrition, and severe plastic deformation. The stability of the nanocrystalline microstructure is discussed in terms of strategies for retardation of grain growth. Selected mechanical properties of nanocrystalline materials are described; specifically strength and ductility. Corrosion resistance is briefly addressed. Examples of present or potential applications for structural nanocrystalline materials are given.

Introduction

This article will attempt to provide an overview of the field of structural nanocrystalline materials.

An important question in this regard is, ‘‘what are the needs for structural nanocrystalline materials?’’. Are there applications for which the superior properties and/or the grain size are required for feasible performance? Are there cases in conventional structural applications where nanostructured materials could be substituted in a cost effective way? This Introduction section will attempt to address these questions for structural nanomaterials in the form of coatings and thin films as well as bulk parts.

Coatings and thin films are applied to structural bulk materials in order to improve the desired properties of the surface, such as wear resistance, friction, corrosion resistance and others, yet keeping the bulk properties of the material unchanged. A typical example is nitriding and carbonitriding of steel parts in order to increase the hardness of the surface and reduce wear.

Modern nanostructured coatings and thin films for structural applications, which were developed during the last 10 to 15 years, are used mainly for wear protection of cutting tools and for the reduction of friction in sliding parts. One distinguishes between nanolayered coatings where a few nanometers thick layers of two different materials are deposited alternately, and nanocomposites which are, in the optimum case, isotropic. The superhard nanocomposites, such as nc-$(Ti_{1-x}Al_x)N$/a-Si_3N_4 (nc- and a- stands for nanocrystalline and amorphous, respectively) show superior cutting performance as compared to conventional, state-of-the-art hard coatings $(Ti_{1-x}Al_x)N$ which presently dominate the applications for dry machining. The costs of their large-scale industrial production are comparable with those of the conventional coatings [1]. Also the heterostructures and multilayers coatings are successfully applied on an industrial scale [2, 3]. Low friction nanostructured coatings consisting of a hard transition metal carbide or nitride in combination with a solid lubricant, such as diamond-like carbon (DLC), MoS_2, WS_2 and others combine high hardness with low friction [4–10]. They are applied in a variety of bearings and sliding parts operating without liquid

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C. C. Koch (✉)
Department of Materials Science and Engineering,
North Carolina State University, Raleigh, NC 27695, USA
e-mail: carl_koch@ncsu.edu

lubricants, which is an important advantage particularly in a hostile environment, and when the movable parts have to stop and go very frequently, as e.g. in the textile industry.

Bulk nanostructured materials are defined as bulk solids with nanoscale or partly nanoscale microstructures. This category of nanostructured materials has historical roots going back many decades but for nanostructured matrices the relatively recent focus is due to new discoveries of unique properties of some nanoscale materials.

Early in the 20th century, when ‘‘microstructures’’ were revealed primarily with the optical microscope, it was recognized that refined microstructures, for example, small grain sizes, often provided attractive properties such as increased strength and toughness in structural materials. A classic example of property enhancement due to a refined microstructure – with features too small to resolve with the optical microscope – was age hardening of aluminum alloys [11]. The microstructural features responsible were first inferred by the X-ray studies of Guinier [12] and Preston [13]. With the advent of transmission electron microscopy (TEM) and sophisticated X-ray diffraction methods, it is now known that the fine precipitates responsible for age hardening, in Al-4% Cu, for example, are clusters of Cu atoms—Guinier–Preston (GP) zones—and the metastable partially coherent θ' precipitate [14]. Maximum hardness is observed with a mixture of GPII (or θ'') (coarsened GP zones) and θ' with the dimensions of the θ' plates, typically about 10 nm in thickness by 100 nm in diameter. Therefore, the important microstructural feature of age-hardened aluminum alloys is nanoscale. Carbide precipitates in certain steels can be nanoscale and affect the mechanical behavior in advantageous ways. Recent development of a cast stainless steel with nanoscale alloy carbides has been found to have exceptional strength and creep resistance at operating temperatures up to 800 °C [15]. The many examples of nanoscale second phases on the strength of structural materials are confined to matrices wherein the grain size is ‘‘conventional’’ that is typically 10s of microns. The focus of recent work is on structural materials where the matrix has a nanoscale grain size.

If nanocrystalline bulk structural materials could be processed in a cost effective manner and scale sufficient for some present structural applications it is clear that with their special, often superior, properties they might supplant existing conventional grain size materials. However, at this stage of development this is not possible. Most methods for preparing truly nanocrystalline materials (grain sizes <100 nm) do not allow for significant quantities or sizes of artifact-free bulk materials at the present time. Major breakthroughs in processing will be needed to accomplish this.

However, some processing methods, to be discussed below in more depth, are capable of producing limited sizes of artifact-free nanostructured materials. What are the potential uses for such small sample sizes? One potential structural application for nanostructured materials comes from the requirements for miniaturization of parts for engineering components for biotechnology, sensors, electro-optics, and micro-nanoscale integration. Material grain sizes must be a factor of 50–100 times smaller than component/feature sizes. Otherwise, mechanical properties will be highly variable and unsuitable for fabrication or end-use. Miniaturization scales <5–10 μm thus require grain sizes <100 nm, that is, nanocrystalline materials. Grain sizes in conventional engineering metals and alloys are typically in the range of 5 to 50 μm which would mean that essentially single crystal behavior would be operative in components of this size. This would lead to large variations in elastic and plastic properties due to the inherent crystallographic differences in behavior. In conventional parts the grain anisotropies are averaged over millions of grains and such variation is not observed. A general guideline for obtaining uniform and predictable properties using polycrystalline materials is that there should be at least 50 grains on the span of a component or feature cross section [16]. When this is the case, the resultant mechanical properties will be the uniform polycrystalline averages expected by the manufacturing engineer.

This paper will then briefly discuss structural nanocrystalline materials from the point of view of their processing, their stability, mechanical properties, corrosion behavior, and current and potential applications.

Processing

Processing of bulk nanostructured materials can in principle be accomplished by either the ‘‘bottom-up’’ assembly of atoms or molecules into nanoscale clusters which require subsequent consolidation into bulk material, or the ‘‘top-down’’ methods which start with a bulk solid and obtain a nanostructure by structural decomposition. The bottom-up methods include the inert gas condensation and compaction technique which stimulated the field. This technique consists of evaporating a metal inside a chamber containing a partial pressure (typically a few hundred Pascals) of an inert gas, e.g. He, such that the evaporated atoms collide with the gas atoms inside the chamber, lose their energy, and condense in the form of small discrete crystals of loose powder. The condensed fine powders collect on a liquid nitrogen cooled cold finger and are stripped off by an annular Teflon ring into a compaction device. The details of this process and improvements to the original design have been published [17]. While this method has provided the materials for the seminal early studies of the properties of nanocrystalline materials, it suffers from both the limited size of samples that can be prepared and from the common problem of two-step methods in that the compaction step may not provide completely dense or bonded material in spite of improvements to the process.

Chemistry is based upon the reactions and manipulations of atoms and molecules and the synthesis of nanocrystalline materials by chemical reactions predates the recent development of this field. Chemical synthesis of nanoscale materials has been reviewed by Chow and Kurihara [18]. In terms of bulk nanostructured materials these methods are two-step in that the particulates formed by the chemical reactions require consolidation. Of course, historically and in the present, the resultant nanoscale particulates can be used as such in applications ranging from catalysts to cosmetic powders. An example of a structural bulk material prepared by chemical reactions is WC-Co. Kear and co-workers [19] have developed a process in which fine and uniform precursor powders are obtained by spray-drying (solvent removal) of homogeneous aqueous solutions of soluble salts of W and Co. This precursor powder is reduced with hydrogen and reacted with CO in a fluidized-bed reactor to yield nanophase WC/Co powder. After consolidation by sintering, the grain size was on the order of 200 nm. These materials provided superior mechanical properties in terms of hardness and toughness compared to larger grain size conventional WC-Co.

Electrodeposition can be classified as a ‘‘bottom-up’’ method of preparation of nanocrystalline materials and also as ‘‘one-step’’ since no consolidation step is needed. Thick electrodeposits may be considered to be bulk materials. Since the late 1980s electrodeposition has been studied as a method to produce nanocrystalline materials and it has moved into the commercial production of such materials. Much of the work was pioneered by Erb and co-workers and this subject has been reviewed by Erb [20]. Using special processing methods, a large number of metals, alloys, composites, and ceramics have been electrodeposited with nanocrystalline microstructures. Electrodeposition occurs by the nucleation of crystallites on the substrate surface and their subsequent growth along with nucleation of new crystallites. In order to obtain a nanocrystalline grain size, nucleation events should be favored over growth. The variables in electrodepostion include bath composition, bath pH, temperature, overpotential, bath additives, and direct current vs. pulse electrodeposition. It has been stated [20] that the two most important mechanisms which are rate-determining steps for formation of nanoscale grains in electrodeposition are charge transfer at the electrode surface and surface diffusion of adions on the crystal surface. One method to inhibit growth of nucleated crystallites is by reducing the surface diffusion of adions by adsorption of foreign species (which may be referred to as ‘‘grain refiners’’ or ‘‘additives’’) on the growing surface. Most such additives are organic materials and may become trapped at the grain boundaries and are presumably responsible for the brittle mechanical behavior observed in nanocrystalline materials processed by electrodeposition with additives. Since high overpotential favors extensive nucleation, pulse plating, as a powerful method to achieve high overpotentials is a technique to synthesize a nanocrystalline structure without the use of additives. In the co-deposition of alloys, the solute ion can act like an organic additive but without the deleterious embrittlement effects. Therefore, there are several processing strategies that can be used to provide artifact-free bulk nanocrystalline materials by electrodeposition. Some of the examples of bulk nanocrystalline materials that exhibit optimized combinations of strength and ductility, to be discussed in the section on properties, were made by electrodepostion.

The ball milling of powders- mechanical attrition- has been a popular method to produce materials with a nanocrystalline grain size [21]. The ball milling of powders can be divided into two categories: (1) the milling of elemental or compound powders—‘‘mechanical milling’’, and (2) the milling of dissimilar powders—‘‘mechanical alloying’’, in which material transfer occurs. This subject has been reviewed by a number of authors [22, 23]. Besides being discussed in the examples of general reviews of ball milling, this specific topic has also been reviewed by itself [21]. Mechanical attrition has been found to refine the grain size to the nanoscale of all solid elements studied. The minimum grain size achieved is dependent upon a number of process and material variables [21]. The minimum grain size obtainable my milling has been attributed to a balance between the defect/dislocation structure introduced by the plastic deformation of milling and its recovery by thermal processes [24]. The minimum grain size is plotted against the melting temperature of the element in Figure 1. At least for the

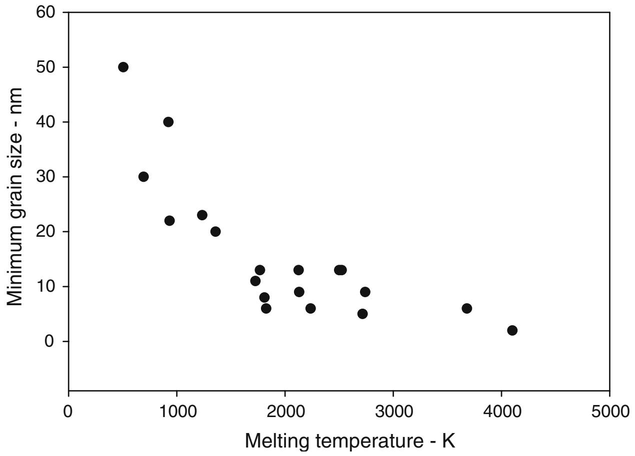

Fig. 1 Minimum grain size as a function of melting temperature for ball milled elements

lower melting metals, there appears to be an inverse dependence of minimum grain size on melting temperature which is consistent with the competition between defect creation and removal. It is clear that mechanical attrition can produce nanocrystalline materials with fine grain sizes such that for higher melting point metals, grain sizes below 10 nm can be achieved. However, in order to attain bulk material, the powders need to be consolidated. The ability to maintain the very small grain sizes in as-milled material and obtain artifact-free bulk samples with minimal grain growth remains a challenge.

For all the ‘‘two-step’’ processes for formation of nanostructured materials the first step provides a nanoscale particulate, or as in mechanical attrition, a powder particle with a nanoscale microstructure. These particulates must then be consolidated into bulk form. The consolidation problem remains an active area for more research and development and has not been adequately resolved to date. The problem is to form by typically a combination of pressure and temperature good atomic bonding between the particulates such that theoretical densities are reached along with the complete interparticle bonding. This should be done without significant coarsening of the nanoscale microstructure or by introduction of any structural defects or unwanted phases. This topic has been reviewed, for example, by Groza [25] and Mayo [26]. Most consolidation methods have used pressure assisted sintering approaches. Shear stresses are most effective in collapsing pores and also disrupt surface oxide layers. Since deformation processes which have significant shear stress components are desired we can list the processes in order of decreasing effectiveness as follows: extrusion—sinter-forging—uniaxial hot pressing—hot isostatic pressing (HIP). Non-conventional consolidation methods for densification of nanocrystalline particulates include microwave sintering, field assisted sintering methods, and shockwave consolidation.

The possibility of producing very fine grain structures by severe plastic deformation was suggested by research using conventional deformation methods taken to very high degrees of strain. It has been known for many decades, going back to the 1950s, that the structure of deformed metals can change with increasing plastic deformation such that random dislocation arrays can lower the energy of the system by ‘‘self assembly’’ into ‘‘cells’’ or ‘‘subgrains’’ such that there is a high dislocation density in the cell walls and a lower dislocation density within the cells. The cells are typically the result of plastic deformation, the cell boundaries are somewhat diffuse. Subgrains, like cells, show small misorietations with their neighbors, but have sharper boundaries, and are formed by plastic deformation and thermal recovery processes. In most cases, the early studies of microstructures produced by severe plastic deformation gave cell or subgrain sizes in the micron down to submicron size scale, but not into the nanoscale. One exception to these results is from the work of Rack and Cohen [27], who reported the cell structure developed in a series of Fe-Ti alloys deformed by wire drawing to large values of true strain up to about 7. The size of the cells decreased with increasing deformation, and reached values of about 50 nm at the highest strains. However, these were all cells with very low angle misorientations. In recent years special methods of mechanical deformation have been developed for producing submicron and even nanoscale grains with high angle grain boundaries. These methods, the microstructure developed, and the properties of the materials with the refined grains so produced have been reviewed by Valiev et al. [28] and form much of the content of this book. The major methods of severe plastic deformation, in addition to mechanical attrition, are severe plastic torsion straining under high pressure (HPT) and equal channel angular pressing (ECAP). In the case of HPT a disk shaped sample is compressed to pressures of about 2 GPa to 6 GPa and then one of the dies is moved with respect to the other. With enough rotation very large values of strain can be achieved, well into the 100s. This method has been used to achieve submicron grain sizes and in some cases even nanocrystalline grain sizes. The ECAP method which allows for the deformation of bulk samples by pure shear was first developed by Segal [29]. In this method a billet is pressed through a die with two channels at angles of intersection typically 90° to 120°. The billet is subjected to severe deformations without changing its dimensions. Multiple passes through the die provide accumulative strain. The grain sizes developed by this method are typically in the submicron, 200 nm to 300 nm, range. A large body of experimental research and modeling studies has been reported for this technique. There are examples of submicron size grain structures induced by the severe strain of ECAP in several metals that provide an excellent combination of both increased strength along with good ductility [30]. Other severe plastic deformation methods which will be described in more detail in the book include accumulative roll-bonding [31] and friction stir welding [32]. It appears that the total strain provided by a given deformation process is in large part responsible for the final grain size that can be obtained. This must be a function of the dislocation density that can be obtained and its subsequent rearrangement by thermal processes. The processes that can provide the highest practical strain levels would be HPT and mechanical attrition of powders. The former has typically been limited to rather small disk samples although recent work is directed to scaling this to larger cylinders [33]. Mechanical attrition typically results in a powder product which then requires consolidation. Recent results on in situ consolidation during ball milling of several ductile metals and alloys have been reported [34]. The processing challenge is to produce nanocrystalline materials with the finest grain sizes to maximize strength, but without artifacts that might compromise ductility, and in sufficient size for mechanical testing and applications.

Stability issues

Knowledge of the thermal stability of nanocrystalline materials is important for both technological and scientific reasons. From a technological point of view, the thermal stability is important for consolidation of nanocrystalline particulates without coarsening the microstructure. That is, many methods, as described above, for synthesis of nanocrystalline materials result in particulate products which must be consolidated into bulk form. Since most consolidation processes involve both heat and pressure, the temperature stability of the nanoscale microstructure is always at risk. The goal of particulate consolidation is to attain essentially 100% theoretical density and good particulate bonding while preventing or minimizing grain growth of the nanocrystalline grains.

Understanding the scientific nature of stability, grain growth of nanocrystalline microstructures is a criterion for allowing strategies for minimizing grain growth to be developed. A basic scientific question with regard to nanocrystalline materials is whether their behavior involves ‘‘new physics’’ or is simply the expected grain size dependent behavior extrapolated to nanocrystalline grain sizes. Thermal stability is an important phenomenon to be addressed in this regard. The thermal stability in a broader sense involves not only the stability of the grain structure, that is the microstructure, but also the stability of the structure of the grain boundaries in nanocrystalline materials. A number of investigations on the thermal stability of nanocrystalline materials have been conducted. Grain growth in nanocrystalline materials has been reviewed by Suryanarayana, [35], Weissmuller, [36], and Malow and Koch, [37].

In spite of the high driving force for grain growth and the observation of grain growth, at least abnormal grain growth, even at very low homologous temperatures, significant stabilization of nanocrystalline grain structures has been observed in many materials. The one common feature of such materials is that they are multicomponent, that is, either alloys or contain impurities. There are two basic ways in which grain growth can be reduced. The first is the *kinetic approach* in which the grain boundaries are pinned in various ways to decrease grain boundary mobility. The second is the *thermodynamic approach* in which the driving force for grain growth is lowered by reducing the grain boundary energy.

In the kinetic approach the grain boundary mobility is reduced by various possible mechanisms. These include porosity drag [38], second phase drag [39], solute drag [40], chemical ordering [41], and grain size stabilization [42]. The thermodynamic approach depends upon the reduction of the grain boundary energy by solute segregation. Since the driving force for grain growth is directly proportional to the grain boundary energy, reducing the grain boundary energy should minimize grain growth. Addition of solute atoms that segregate to the grain boundaries will affect the grain boundary energy. This concept has been modeled by Weissmuller [43, 44], Kirchheim [45], and Liu and Kirchheim [46]. The grain size at the metastable thermodynamic equilibrium was found in their analysis to be determined by the grain boundary energy, the enthalpy change of grain boundary segregation, and the solute excess of an equivalent grain boundary monolayer at saturation. Good agreement for these predictions of the temperature dependence of the metastable grain size was obtained for $Pd_{100-x}Zr_x$ alloys [46]. This is illustrated in Figure 2. The thermodynamic approach to grain size stabilization by segregation of solute, impurity atoms to the grain boundaries appears to be an effective method for stabilization of nanocrystalline grain size. However, in terms of mechanical behavior it is not yet clear whether such grain boundary segregation will not always lead to an embrittlement of the alloy. More research is needed on this topic.

Mechanical properties

One of the areas of research on nanocrystalline materials that has received extensive study is their mechanical behavior. The great interest in the mechanical behavior of nanocrystalline materials originates from the unique mechanical properties first observed and/or predicted by the pioneers of this field, Gleiter and co-workers [47] Among these early observations or predictions were:

- Lower elastic moduli than for conventional grain size materials—by as much as 30—50%.
- Very high hardness and strength—hardness values for nanocrystalline pure metals (~10 nm grain size) that are 2 to 10 or more times higher than those of larger grained (>1 μm) metals.
- Increased ductility—perhaps even superplastic behavior—at low homologous temperatures in even normally brittle ceramics or intermetallics with nanoscale grain sizes, believed due to grain boundary, diffusional deformation mechanisms.

While some of these early observations and predictions have been verified by subsequent studies, in particular the high hardness and strength values, some have been found to be due to high porosity in the early bulk samples (for example the low elastic moduli observed) or to other processing artifacts, and not inherent properties of the nanocrystalline materials. The ductility issue remains a subject of present research, and while most nanocrystalline materials don't exhibit the high predicted ductilities and in fact show little ductility in tension [48] there are recent examples of good ductility along with high strength in a limited number of cases [49–51].

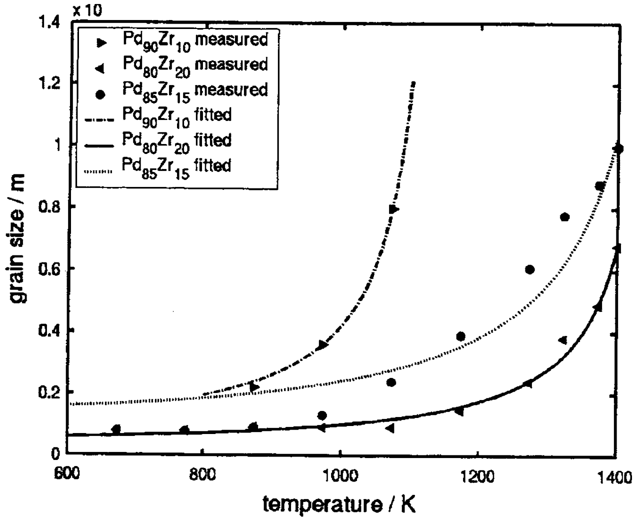

Fig. 2 Theoretical fits of grain size vs. annealing temperature for nanocrystalline $Pd_{100-x}Zr_x$ alloys (after Liu and Kirchheim [46])

Three major limitations to ductility for nanocrystalline materials can be identified. These are: (1) artifacts from processing; (2) force instability in tension; (3) crack nucleation or propagation instability. Porosity was a major artifact, especially for earlier studies of metals made by the inert gas condensation method. Even when theoretical density is attained, complete particle bonding may be lacking. Nanocrystalline materials made by ball milling of powders also can suffer from lack of complete bonding after power consolidation. The surfactant that is sometimes used to prevent excessive cold-welding during milling can prevent complete bonding during consolidation and therefore limit ductility. Another popular method for producing nanocrystalline materials is electrodeposition. While this method is ''one-step'' in that it does not require consolidation of particulates and the problems associated with this, most of the nanocrystalline materials made by electrodeposition have also exhibited very poor ductility presumably due to the additives often used to attain a nanocrystalline microstructure, as discussed in Section 2. However, as will be described below, several examples of high strength and good ductility are observed with electrodeposited nanocrystalline materials produced without the use of organic additives.

Necking generally begins at maximum load during tensile testing. The amount of uniform elongation depends upon the strain hardening such that true uniform strain ε_u = n in a cylindrical specimen (or ε_u = 2n for a sheet) where n is the strain hardening coefficient. For an ideally plastic material (such as amorphous alloys) where $n = 0$, the necking instability would begin just as soon as yielding occurred. This criterion implies that the sample is mechanically stable until the rate of strain hardening falls to a level determined by the flow stress (and prior strain) at that time. Materials with a high capacity for strain hardening are therefore stable, while those with little capacity for strain hardening are potentially unstable.

Elongation to failure in tension is plotted vs. grain size in Figure 3 for a variety of metals and alloys. It is clear that for most metals with grain sizes below about 30 nm the elongation to failure values are very low, typically less than 2–3%. Since this graph was originally published [48] several new datum points have been added that show significant ductility for grain sizes of ≤30 nm. These more recent breakthroughs in ductility will be described below.

As described above, strain hardening is needed in order to minimize mechanical instabilities that lead to local deformation (necking) and failure. The ability to strain harden therefore becomes an important criterion for ductility in nanostructured materials. An approach that has been used to provide strain hardening in nanostructured materials is to introduce a bimodal grain size distribution by appropriate processing methods. The supposition was that the larger grains should deform by the usual dislocation mechanisms and provide strain hardening, while the smaller nanoscale grains would provide the strength and hardness.

Results of Ma and co-workers [52] have provided a dramatic example of combinations of high strength and high tensile ductility. Copper was rolled at liquid nitrogen temperature to high strains of 93 % to create a high dislocation density that does not dynamically recover. The as-rolled microstructure showed the high dislocation density along with some resolvable nanoscale grains with dimensions less than 200 nm. Annealing for short times at temperatures up to 200 °C provided for the development of grains with high angle boundaries that were in the nanoscale or submicron size range. Some abnormal recrystallization was observed such that for annealing at 200 °C for 3 min, about 25% volume fraction of the samples consisted of grains 1–3 μm in diameter. Rolling the Cu at room temperature did not provide sufficient dislocation density to accomplish the subsequent nanoscale/submicron grain sizes on annealing. This work on Cu gave stress–strain curves for annealed coarse-grained Cu, Cu rolled to 95% at room temperature, Cu rolled to 93% at liquid nitrogen temperature, and these samples annealed for 3 min at either 180 °C or 200 °C. The optimum properties were obtained for the mixed grain size material with the 1–3 μm grains imbedded in the matrix of nanoscale and submicron size grains. This material had a high yield stress of about 340 MPa, a total elongation to failure of 65% and uniform elongation of about 30%. The ductility was thus comparable to that of annealed conventional grain size Cu, but the yield strength was almost 7 times higher.

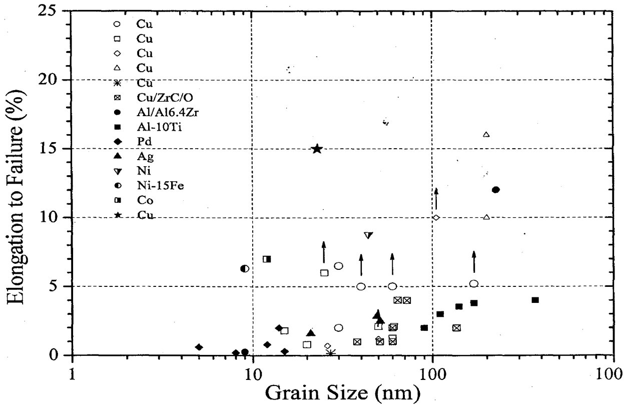

Fig. 3 Elongation to failure in tension versus grain size for a variety of metals and alloys

Lavernia and co-workers have prepared a commercial Al alloy, 5083 [53] and an Al-7.5%Mg alloy [54] by cryomilling followed by powder compaction by hot isostatic pressing and extrusion. The cryomilling of Al alloy 5083 [53] resulted in a nanoscale microstructure with average grain size about 30 nm. After hipping and extrusion the grain size remained mostly nanoscale at an average value of about 35 nm. However, some larger grains were also observed in the TEM analysis. The stability of the nanoscale grain size during the elevated temperature compaction steps was attributed to the large number of various precipitates including several intermetallic compounds such as Mg_2Si and Al_3Mg_2 as well as compounds formed from interstitial impurity atoms, namely AlN and Al_2O_3 which presumably retard grain growth by Zener pinning of the grain boundaries. A few larger micron size grains were formed by secondary recrystallization. These large grains were believed to be responsible for the good ductility observed in these materials along with large increases in strength. Guided by these results, an Al-7.5% Mg alloy was cryomilled to nanostructured grain sizes [54]. The cryomilled powder was then combined with either 15 or 30% by volume of unmilled alloy powder, which was made by powder atomization and had micron scale grain sizes. The powders were then consolidated by hipping and extrusion to bulk samples for tensile testing. The additions of larger grains to the nanocrystalline matrix increased the tensile ductility from about 1.4% to 5.4% elongation, with some decrease in strength values but still about four times the yield strength of conventional Al 5083.

While nanoscale grain boundaries have been the focus for increasing strength in studies of nanocrystalline materials, twin boundaries can also be an effective obstacle to dislocation motion and a potent strengthener. Lu and co-workers [55] have reported the synthesis of nanoscale growth twins in electrodeposited Cu. The Cu grain sizes were of the order of 400–500 nm and the twin lamellae thicknesses ranged from averages of about 100 nm down to <20 nm. The yield strength of the Cu followed Hall–Petch behavior with increased strength as twin lamellae spacing decreased. Increased ductility also was observed with decreasing twin lamellae spacing. The Cu with the finest twin lamellae spacing shows both high strength and ductility. Higher strain hardening than conventional grain size Cu is also noted.

While some strategies for optimization of strength and ductility, such as bimodal grain size distributions, compromise some strength for ductility, there are several recent results on nanostructured materials where strength levels are high and good ductility can still be achieved. These results are for nanocrystalline materials with small grain sizes (<30 nm) and with relatively narrow grain size distributions such that no grains >50 nm are present.

Electrodeposited Co metal has been prepared with a small average grain size of about 12 nm and with a fairly narrow grain size distribution of ±7 nm [49]. This material had the hcp structure with no trace of the fcc phase, that is, it had the equilibrium structure for room temperature. The hardness, yield strength, and ultimate tensile strength for this nanostructured Co were 2–3 times higher than for conventional grain size Co. The nanocrystalline Co exhibited elongation to fracture values of 6 to 9% which are comparable to those for the conventional grain size Co. Of great interest is the dependence of the mechanical behavior of the nanostructured Co on the strain rate of the tensile tests. Applying lower strain rates resulted in higher flow stress and tensile strength at relatively constant yield strength. This behavior is in contrast to the usual response of a material in which dislocation slip is the dominant mechanism. In such materials higher strain rates result in higher tensile strength. The authors suggest this response of nanocrystalline Co to changes in strain rate are typical of materials which deform predominantly by deformation twinning. That is, higher strain rates result in lower flow stress and tensile strength. They therefore suggest that the dominant deformation mechanism in their nanocrystalline Co is twinning. More studies, in particular high resolution TEM or in situ TEM under stress, are needed to confirm these ideas about twinning deformation.

Li and Ebrahimi [50] have prepared nanocrystalline Ni and Ni–Fe alloys by electrodeposition without the use of any additives that might induce embrittlement. Their samples exhibited excellent strength values along with good ductility. The Ni sample had a grain size of 44 nm and the Ni—15% Fe sample had a 9 nm grain size. The fracture behavior of the alloys was very different even though both exhibited good values of % elongation. The Ni sample had a % elongation of about 9% and also showed significant reduction of area and ductile fracture behavior consistent with that for other ductile fcc metals and deformation by dislocation motion. While the Ni—15% Fe sample also showed reasonable % elongation of about 6%, the reduction in area was negligible and fracture appeared to be brittle. TEM revealed grain boundary cracking. The authors suggest that the Ni—15% Fe alloy with the average grain size of 9 nm was below the ‘‘cross-over’’ grain size from dislocation dominated deformation processes to grain boundary deformation processes such as grain boundary sliding. In spite of this apparent brittle fracture behavior good ductility along with high strength were observed suggesting processing artifacts did not affect the mechanical properties.

The in situ consolidation of ball milled powders in several metals has allowed for the production of artifact free samples for tensile testing. Bulk nanocrystalline Cu spheres were synthesized using a combination of liquid nitrogen temperature and room temperature milling [34, 51]. Spheres with diameters up to about 8 mm were obtained that could be pressed into disks from which samples for mechanical testing could be machined. TEM results shown in Figure 4a indicate that the consolidated Cu consists of equiaxed nanograins oriented randomly, as can be seen from the corresponding selected area diffraction pattern, the upper left inset in Figure 4a. Statistical analysis of multiple dark field images reveals a monotonic lognormal grain size distribution with an average grain size of 23 nm (Figure 4b). Density measurements, scanning electron microscopy of the sample surfaces, and TEM analysis show that no porosity is introduced during the in situ consolidation of nanocrystalline Cu. The chemical analysis of the consolidated nanocrystalline Cu indicated that the oxygen content increased from 0.10 at. % in the starting powder to 0.29 at. % in the final product. The measured Fe contamination was less than 0.1 at. %. Therefore, it may be concluded that the nanocrystalline Cu made by the above procedure is free of artifacts in that there is no porosity, no debonding, and minimal impurity contamination.

Tensile test data for the *in situ* consolidated nanocrystalline Cu is compared with the stress–strain curve for conventional grain size Cu in Figure 5 [51]. In the case of the nanocrystalline Cu, the 0.2% offset yield strength (σ_y) and the ultimate tensile strength (σ_u) reach values of 971 ± 12 MPa and 1120 ± 29 MPa respectively. This σ_y value is at least one order of magnitude higher than that of coarse-grained pure Cu samples, and σ_u of the nanocrystalline Cu is about five

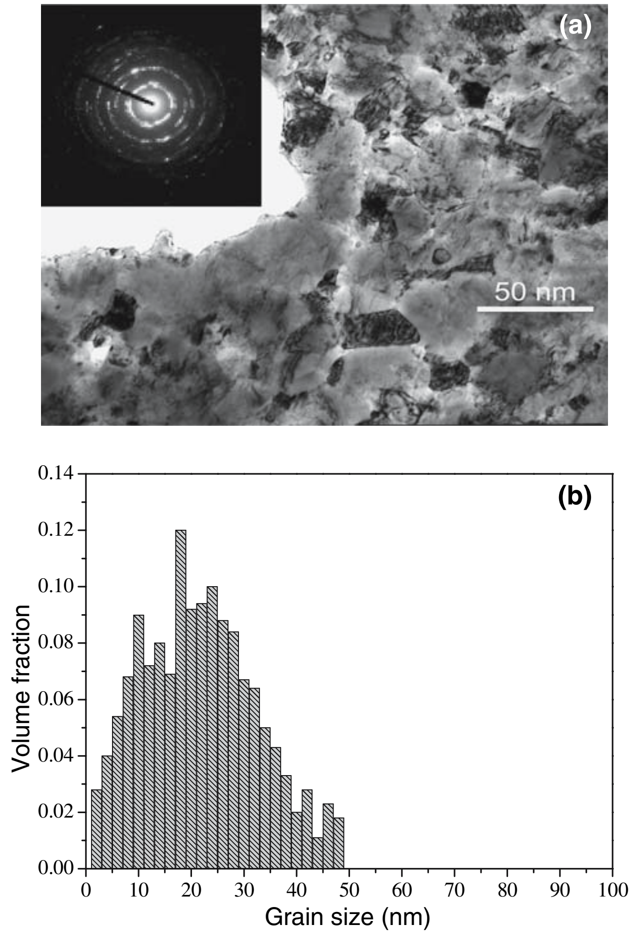

Fig. 4 TEM observations of the typical microstructure in the in situ consolidated nanocrystalline Cu. The bright-field TEM micrograph (**a**) and the SADP [the upper left inset in A] show roughly equiaxed grains with random orientations. The statistical distribution of grain size (**b**) was obtained from multiple dark-field images of the same sample [51]

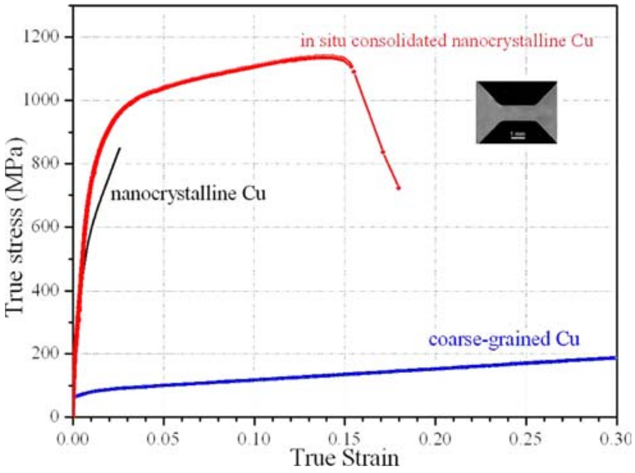

Fig. 5 Stress–strain curves for *in situ* consolidated nanocrystalline Cu, nanocrystalline Cu made by the inert gas condensation method, and coarse-grained Cu [51]

times higher than that of the coarse-grained Cu sample. The hardness value of this nanocrystalline Cu is 2.3 GPa, which is consistent with the Hall–Petch behavior of Cu. Therefore, it is concluded that the high values of hardness and yield strength are due to the small grain size (23 nm). These strength values are comparable to the highest values observed for nanocrystalline Cu but more significant is the good tensile ductility observed with 14 % uniform elongation and 15 % elongation to failure. This ductility is much greater than previously reported for nanocrystalline materials of this grain size and even somewhat greater than the ductility of the nanotwinned Cu [55]. Another important feature of the stress–strain curve (Figure 5) is the large strain hardening observed in the plastic region which suggests a high lattice dislocation accumulation during the plastic deformation up to failure. Strain hardening is often limited in nanocrystalline materials at grain sizes where dislocation activity is believed to be difficult. *In situ* dynamic straining transmission electron microscope observations of the nanocrystalline Cu were also carried out, which showed individual dislocation motion and dislocation pile-ups. This suggests a dislocation-controlled deformation mechanism that allows for the high strain hardening observed. Trapped dislocations were also seen in individual nanograins.

An artifact-free bulk nanocrystalline Al-5% Mg alloy was also prepared using *in situ* consolidation during ball milling at liquid nitrogen and room temperatures [56]. The average grain size, determined by TEM, was 26 nm with a relatively narrow grain size distribution. The nanocrystalline structure produced was a supersaturated solid solution of Mg in Al. The tensile behavior of the nanocrystalline alloy showed an extremely high strength. The tensile yield strength reached 620 MPa (four times that of the coarse-grained Al-5083 alloy), and the ultimate tensile strength was 740 MPa. A significant tensile ductility was obtained with an elongation to failure value of 8.5%. Strain hardening was also observed which is suggested to originate from dislocation accumulation during plastic deformation.

Corrosion resistance

An important attribute for any structural material is its resistance to corrosion. Metallic structural materials typically degrade when exposed to certain environments and it is well known that the economic losses due to corrosion are significant in industrialized nations. If nanocrystalline materials are to be used in structural applications, their resistance to corrosion needs to be determined. From conceptual points of view, nanocrystalline materials would appear to have both possible disadvantages and advantages with regard to corrosion resistance compared to conventional grain size materials. The large grain boundary area of nanocrystalline materials would suggest poor corrosion resistance since grain boundary sites are known regions for the initiation of corrosion. On the other hand, it has been pointed out that for alloys with elements which are capable of forming passive films, the atoms of these elements can diffuse easily through the grain boundaries to the surface of the alloy to form the protective passive layer. In fact, from the limited number of studies reported on the corrosion behavior of nanocrystalline materials both decreased and increased corrosion resistance have been noted. Rofagha et al. [57] investigated the corrosion behavior of nanocrystalline and coarse-grained Ni in sulfuric acid media. They found that coarse-grained Ni exhibits passivation behavior, but no passivation behavior was observed for the nanocrystalline Ni. In contrast to these results, Zeiger et al. [58] reported enhanced corrosion resistance of nanocrystalline Fe-8 wt.% Al in Na_2SO_4 solution (pH = 6). Other reports of decreased [59–61] or increased [62–65] corrosion resistance for nanocrystalline materials have been presented. While there is still limited data on the corrosion resistance of nanocrystalline materials, a few generalizations may be made. It appears that under severe corrosion conditions (e.g. low pH values) general corrosion can be much greater for nanocrystalline materials than for the conventional grain size counterpart. However, less localized, pitting corrosion can result from a nanocrystalline microstructure. The corrosion behavior, as with conventional materials, is very material specific and depends strongly on the nature of the passive film that can form. Much more research needs to be done on the corrosion behavior of nanocrystalline materials to clarify these limited observations.

Applications

Some present or potential applications of nanocrystalline materials for structural applications have been briefly described in the Introduction section. These included nanocrystalline superhard thin film coatings and nanocrystalline materials for miniaturization of structural components. Nanoparticles or carbon nanotubes have been used as reinforcements to improve the mechanical properties of metal matrix composites and polymer matrix composites. Special attention has been devoted to the use of exfoliated nanoscale clay flakes as fillers for polymer structural materials. In the remainder of this section examples of the present or potential use of nanocrstalline materials for structural applications will be given for electrodeposited nanostructures and structural nanomaterials for military applications.

Applications of electrodeposited nanostructures

Electrodeposited nanocrystalline materials can be in the form of thick coatings, free standing foils, plates, or tubes so can be considered to be bulk structural materials. Palumbo et al. [66] have reviewed the applications for electrodeposited nanostructures. These authors list a wide variety of applications, some already in commercial use, some potential. One example of a large-scale structural application of a bulk nanostructured material was the use of an electrodeposited Ni microalloy as an in situ repair technique for nuclear steam generator tubing [67]. Electrodeposited bulk nanostructured Ni and Co alloys have been recently developed as environmentally benign replacements of hard Cr electroplating [68]. Microelectromechanical structures (MEMS) have been produced by an electrodeposition molding technique (through-mask electroplating, or LIGA, originally developed in Germany). The LIGA method uses photoresist technology to fabricate high aspect ratio components. However, conventional MEMS components made by LIGA suffer from the anisotropy of properties due to the large columnar grains formed by the conventional electrodeposition. Severe reliability problems can occur because of the anisotropic mechanical properties such as elastic modulus and strength that occur for different grain orientations when only a few grains make up the MEMS component. It has been shown that nanostructured MEMS components exhibit considerably improved cross-sectional properties both in terms of uniformity (hardness and elastic modulus) and overall hardness level.

Potential military applications

Nanocrystalline materials, due to the possible combination of high strength and good ductility, can be tough. It is claimed that Ni–Fe armor plating can be twice as tough as the required specifications for military vehicles when made in nanocrystalline form. [69].

Electromagnetic launchers, rail guns, use the electrical–magnetic energy to propel penetrators/projectiles at velocities up to 2.5 km/s. This increase in velocity over conventional explosives can deliver projectiles with an impact velocity of Mach 5 to targets at ranges of 250 miles. Since a railgun operates on electrical energy, the rails need to be very good conductors of electricity. They also need to be strong and rigid so that the railgun does not sag while firing and buckle under its own weight. While a good electrical conductor like Cu might be the choice for the rails, Cu is too weak and does not have sufficient wear resistance or high temperature strength. Therefore, nanocomposites of W, Cu, and TiB_2 are being studied which may provide the combination of good electrical conductivity and strength required [70].

Kinetic energy penetrators made from nanocrystalline bcc metals such as tungsten heavy metal alloys are being evaluated for possible replacement of depleted uranium projectiles. Plastic flow localization has been studied in bulk tungsten with an ultrafine grain structure [71]. This shear localization is not found in conventional grain size tungsten, and is responsible, along with crack formation, to discard material in the ‘‘self-sharpening’’ penetration which is desired.

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