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TOP-DOWN SYNTHESIS OF NANOSTRUCTURED MATERIALS: MECHANICAL AND THERMAL PROCESSING METHODS

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Abstract. This paper reviews the "top-down" methods for synthesis of nanostructured or submicron grain size materials which utilize severe plastic deformation along with thermal processes. Of the variety of methods discussed, it appears that only ball milling, high pressure torsion, and accumulative roll bonding can regularly produce average grain sizes below 100 nm – that is, nanocrystalline materials. Recent examples of combining conventional deformation processing methods with annealing show the possibility of forming nanocrystalline/submicron grain sizes that can optimize mechanical properties in practical ways.

1. INTRODUCTION

Nanostructured materials, which can be defined as materials with crystallite sizes less than 100 nm in dimension, are synthesized by either "bottom-up" or "top-down" processes [1]. The bottom-up approach starts with atoms, ions or molecules as "building blocks" and assembles nanoscale clusters or bulk material from them.

The "top-down" methods for processing of nanostructured materials involve starting with a bulk solid and obtaining a nanostructure by structural decomposition. One such approach involves the lithography/etching of bulk material analogous to the processes used in the semiconductor industry wherein devices are formed out of an electronic substrate by pattern formation (such as electron beam lithography) and pattern transfer processes (such as reactive ion etching) to make structures at the nanoscale. This broad area will not be covered further in this paper. The main subject of this paper will be the preparation of nanostructured materials from the bulk by the use of mechanical/thermal methods. The major methods to be discussed use severe plastic deformation to introduce defects, i.e. dislocations, into the material which can then "self-assemble" into nanoscale grains, with or without the aid of external thermal sources. In the remainder of the paper the various methods for processing nanostructured materials in these ways will be described and discussed. This will include examples from the author's laboratory as well as from the literature. The nature of the microstructural evolution which provides the sought-for nanoscale structures will also be discussed with respect to possible mechanisms.

2. PROCESSING METHODS

2.1. Ball milling and consolidation of powders

The ball milling of powders was first developed as a powder metallurgy method to produce dispersion strengthened alloys with fine, uniform dispersoid distributions [2]. Subsequently, it has been used as a powerful nonequilibrium processing method that can synthesize a variety of metastable structured materials. The ball milling of powders – mechanical attrition – can be divided into two categories: 1. the milling of elemental or compound powders – "me-

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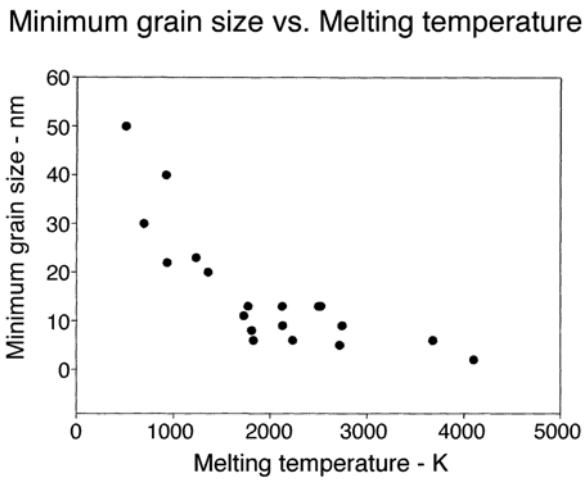

Fig. 1. Minimum nanocrystalline grain size for ball milled elements *vs*. their melting temperature. Data from references 7, 9, 10, 11.

chanical 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, *e.g.* [3-5]. Nanostructured materials are one class of metastable materials that can be made by ball milling. Besides being discussed in the examples of general reviews of ball milling, this specific topic has also been reviewed by itself, *e.g*. [6-8]. The details of the mechanical attrition processes, equipment used, *etc.* have been covered in a number of reviews, *e.g*. [4], and will not be repeated here.

Mechanical attrition has been found to refine the grain size to the nanoscale of all solid elements studied. The minimum grain size achieved is, however, dependent on a number of process variables as well as properties of the element or alloy. The minimum grain size obtainable by milling, d_{min}, has been attributed to a balance between the defect/dislocation structure introduced by the plastic deformation of milling and its recovery by thermal processes [9]. It has been found that the minimum grain size induced by milling scales inversely with the melting temperature of a group of fcc structure metals studied [9]. These data are plotted in Fig. 1 along with data for other metals and carbon (graphite) [7]. For these data, only the lower melting point metals show a clear inverse dependence of minimum grain size on melting temperature. The minimum grain size for elements with higher melting temperatures ($>T_M$ for Ni), exhibit essentially constant values with melting temperature for given crystal structure classes. For these elements it appears that d_{min} is in the order: fcc < bcc < hcp. However, these data must be considered with some skepticism since they were obtained by several different research groups using different milling equipment, and the measurements of grain size were mainly by the analysis of x-ray diffraction line broadening, which can be questionable in terms of absolute values. In spite of these potential problems, however, the values for d_{min} are in remarkable agreement between the data of Fecht *et al.* [10] who used a high energy shaker mill (Spex 8000) and that of Olesak and Shingu [11] who used a conventional horizontal low energy ball mill. These results suggest that total strain, rather than milling energy or ball-powder-ball collision frequency, is responsible for determining the minimum nanocrystalline grain size. This is different from ball milling induced amorphization or disordering where it appears the energy and frequency of ball-powder-ball collisions determine the final structures formed in "driven systems". It is, however, consistent with observations of nanocrystallites formed at high strain values using other non-cyclic deformation methods, as will be discussed later in this paper. These results suggest that mill energy per se is not critical to the final microstructure, but of course, the kinetics of the process are dependent on the energy, and times for attaining the same microstructure can be several orders of magnitude longer in the low energy mills than in high energy mills.

Effect of Milling Temperature. Milling temperature has been observed to affect the rate at which the nanocrystalline structure develops. The milling time at which a given grain size was attained in a TiNi intermetallic compound was a function of milling temperature, with smaller grains formed at lower milling temperatures [12]. Shen and Koch [13] also observed smaller nanocrystalline grain sizes in both Cu and Ni milled at -85 °C compared to samples milled at room temperature. For example, for Cu, $d = 26 \pm 3$ nm for room temperature milling and $d = 17 \pm 2$ nm for milling at -85 °C. Evidence for smaller nanocrystalline grain sizes formed by milling at low temperatures have now been observed in a number of materials including the intermetallic compound CoZr [14] and elemental Zn [15]. Since milling at temperatures lower than ambient can bias the defect accumulation induced by plastic deformation with respect to thermal recovery, higher dislocation densities, and therefore, as observed, finer grain sizes can be obtained. The first uses of milling at cryogenic temperatures, however, have been for the purpose of introducing fine nanoscale nitrides or

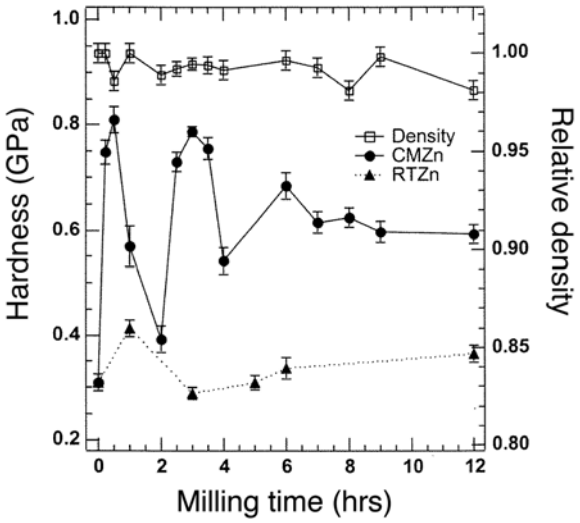

Fig. 2. Hardness vs. milling time for cryomilled Zn (solid circles) and Zn milled at room temperature (solid triangles). The relative density for the cryomilled samples is shown by the open squares. Reference 19.

oxynitrides into Al [16]. This method has subsequently been used to similarly dispersion harden other materials including NiAl [17] and Inconel 625 [18]. In this case, liquid nitrogen is introduced into the milling vial along with the powders and milling balls. The chemical reaction of the nitrogen with the metal matrix powders produces the fine nitride particles which can help stabilize the nanoscale grain size during subsequent thermal/mechanical powder consolidation, as well as serve as dispersion hardening agents.

A recent study of the milling of Zn at cryogenic temperatures, albeit with the Zn milled under an argon atmosphere, has revealed a modulated cyclic variation in hardness/strength with milling time which has implications on the formation mechanisms for nanocrystalline grain sizes by plastic deformation [19]. The measured density and hardness values for cryomilled Zn are shown in Fig. 2 as a function of milling time. The hardness values for Zn milled at room temperature are also shown. A relative density greater than 98% of theoretical density was obtained for all of the Zn samples after milling and powder compaction. The magnitude of the hardness peaks decreases with milling time, thus exhibiting a modulated oscillatory hardening manifest as damped oscillations of the hardness. At longer milling times the hardness reaches a steady-state value about twice that of unmilled Zn. Transmission electron microscopy showed that large variations in the dislocation density and grain-size distribution occurred during cryomilling. The observations suggest that dynamic recrystallization takes place in larger grains when the dislocation density due to strain-hardening reaches a critical level. A reaction-rate model was developed which accounts for the dynamic recrystallization effect and the observed oscillations in hardness.

Proposed Mechanisms for Formation of Nanostructures by Ball Milling. The first description of the formation of nanocrystalline materials by mechanical attrition was given by Fecht *et al.* [10]. The observed phenomenology of nanocrystallization by mechanical attrition was summarized as occurring in three stages, namely:

- Stage 1. Deformation localization in shear bands containing a high dislocation density.
- Stage 2. Dislocation annihilation/recombination/rearrangement to form cell/subgrain structures with nanoscale dimensions – further milling extends this structure throughout the sample.
- Stage 3. The orientation of the grains becomes random, that is, low angle grain boundaries disappear as high angle grain boundaries replace them, by presumably grain boundary rotation/sliding.

Stage 2 might be considered to be a form of self-assembly since the dense dislocation arrays form into subgrain boundaries in order to lower the energy of the system. This mechanism proposed by Fecht and co-workers appears to be a logical description, and may in most cases be the process of nanocrystallization. However, from the results on cryomilled Zn discussed above, in some special cases high angle nanocrystalline grains can also be formed by a “discontinuous” dynamic recrystallization process in contrast to the continuous rearrangement of dislocation structures during deformation which leads to subgrains and then grains with high angle boundaries.

Nanocrystalline grains are observed during the mechanical alloying of dissimilar component powders. Klassen et al [20] followed the phase formation and microstructural development during mechanical alloying of Ti and Al powder blends of overall composition $Ti_{25}Al_{75}$. TEM revealed nanocrystalline grains of partially ordered $L1_2$ phase with a crystallite size of 10-30 nm in the alloy layers at the interface between the pure Ti and Al lamellae at very early stages of the milling process. The alloy phase which develops between the pure powder components consists of nanocrystalline grains presumably because of the multiple nucleation events

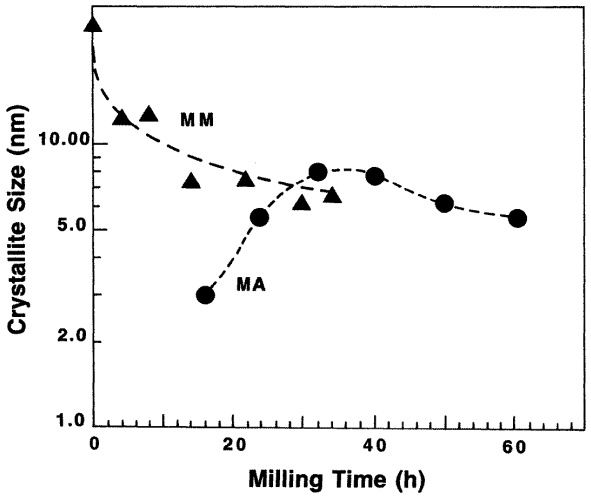

Fig. 3. Crystallite size for FeTi intermetallic phase for low energy mechanical alloying of Fe and Ti powders (solid circles), and mechanical milling of the FeTi compound powders (solid triangles) [21].

and the slow growth which occur at the relatively low temperatures (100 – 200 °C above ambient) during milling. Trudeau *et al.* [21] prepared nanocrystalline FeTi by both low milling energy mechanical alloying of elemental Fe and Ti powders, and by mechanical milling of FeTi compound powders. Higher mill energies resulted in amorphization. The grain size of the mechanically milled FeTi steadily decreased with milling time while that for the mechanically alloyed Fe/Ti first increased and then decreased to values essentially identical to those for the milled samples. This effect is illustrated in Fig. 3.

It might be expected that brittle components would simply fracture during milling and be reduced in size to the limit of comminution observed in the grinding of brittle mineral powders. However, it has been found that ball milling of some nominally brittle materials can lead to alloying of the brittle components, *e.g.* Si and Ge [22] and the introduction of significant plastic deformation and high dislocation densities in brittle compounds, *e.g.* Nb_3Sn [23]. Si and Ge are completely brittle at room temperature and yet complete solid solutions of Si-Ge alloys were obtained across the binary phase diagram. Thus, alloying on the atomic scale was observed by mechanical alloying of brittle components. Nb_3Sn is an extremely brittle intermetallic compound which fractures elastically until tested at temperatures above about 1400 °C. However, ball milling Nb_3Sn can produce large amounts of plastic deformation as observed by TEM of the milled powder. The dislocations so produced then presumably induce a nanocrystalline grain structure similar to that formed in milled ductile metals. It is not yet clear how ball milling can produce large plastic deformation in materials that are very brittle under uniaxial stress conditions. It is suggested that the high hydrostatic stress component that may exist in the powders during milling can favor plastic deformation over fracture and allow a large dislocation density to be generated [23]. Mechanical attrition has also been found to induce nanocrystalline microstructures in brittle ceramics such as ZrO_2 and ceramic powder mixtures such as Fe_2O_3/Cr_2O_3 and ZrO_2/Y_2O_3 [8].

Ball Milling of Polymeric Materials. The application of mechanical attrition to polymeric materials was initiated by Shaw and co-workers [24]. In order to fracture the polymer particulates, and on the microscopic level the polymer chains, the milling was conducted at temperatures below the glass transition temperature of the given polymer. Shaw's group has studied a number of homopolymers such as polyamide, polyethylene, acrylonitrile-butadiene-styrene, polypropylene, and polystyrene. Refinement of the microstructure typically occurred and milling-induced structural and property changes were noted that were very material specific. Subsequently, others have studied milling-induced changes in the structure of several semi-crystalline and amorphous homopolymers [25]. Milling of poly(methyl methacrylate) (PMMA) resulted in monotonic decreases in molecular weight and glass transition temperature, reflecting the milling-induced scission of the polymer chains. Polyisoprene (PI) exhibited much different behavior in that the decrease in glass transition temperature, T_g, given by $\Delta T_g = T_{g,0} - T_g(t_m)$, where $T_{g,0}$ is the glass transition temperature of the unmilled polymer and t_m is the milling time, first increased and then decreased as illustrated in Fig. 4. In this case cryomilled PI does not exhibit a monotonic increase in ΔT_g but instead shows a sharp maximum at relatively short milling times (2h) followed by a drop to almost zero before again increasing slightly for longer milling times. This unusual, but reproducible, behavior strongly suggests that the PI chains undergo chemical crosslinking during cryomilling. In this case we imagine a dynamic competition between chains breaking (causing a decrease in molecular weight) and crosslinking (promoting an increase in molecular weight) under the nonequilibrium conditions of milling. Sol-gel analysis and FTIR spectroscopy gave

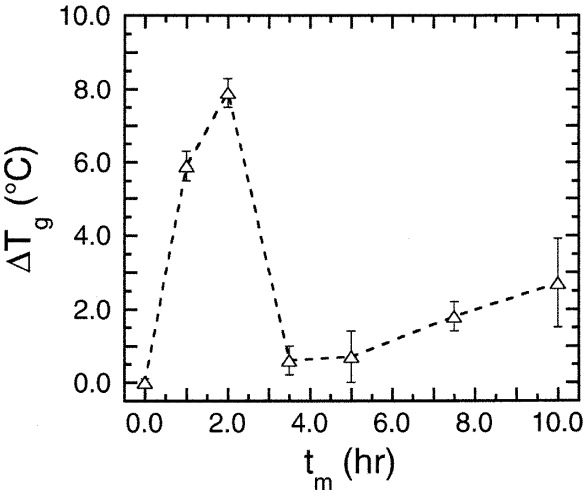

Fig. 4. Dependence of ΔT_g on milling time, t_m, for cryomilled polyisoprene. Reference 24.

further evidence for the milling-induced crosslinking in PI. Mechanical attrition was also performed at cryogenic temperatures to incorporate PI into PMMA [26]. TEM clearly showed that the solid-state blending by mechanical attrition of polymeric materials can yield nanoscale dispersions of immiscible polymers. The strong evidence for free radical formation and crosslinking induced by milling suggests many possibilities for the design of novel new polymeric materials with nanoscale microstructures.

Problems: Contamination and Powder Consolidation. A serious problem with the milling of fine powders is the potential for significant contamination from the milling media (balls and vial) or atmosphere. If steel balls and containers are used, iron contamination can be a problem. It is most serious for the highly energetic mills, for example, the Spex shaker mill, and depends upon the mechanical behavior of the powder being milled as well as its chemical affinity for the milling media. For example, milling Ni to attain the minimum grain size in a Spex mill resulted in Fe contamination of 13 at.%, while the Fe contamination in nanocrystalline Cu similarly milled was only <1 at.% [27]. Lower energy mills result in much less, often negligible, Fe contamination. Other milling media, such as tungsten carbide or ceramics can be used but contamination from such media is also possible. Interstitial element (oxygen, nitrogen) contamination can be controlled by milling and subsequent powder handling in a pure inert gas atmosphere, with care taken that the milling vial is leak-free during processing.

Powder consolidation to theoretical density of nanocrystalline materials prepared by mechanical attrition without significant coarsening of the microstructure is necessary for many property measurements, for example, mechanical behavior, and for applications that require bulk materials. There is not room in this paper to adequately review the increasing effort in this important area. However, research on particulate consolidation in this regard by both conventional (*e.g.* hot pressing, hot isostatic pressing, extrusion, *etc.*) and innovative methods (*e.g.* microwave sintering, plasma activated sintering, *etc.*) has been documented and is reviewed by Groza [28]. For the special case of very ductile, relatively low melting temperature metals such as Zn, it has been found that in the absence of a process control agent during milling, the cold-welding can dominate the process such that the powders can be "consolidated" during milling into spherical shaped balls that can be up to 6 – 10 mm in diameter [29]. Thus, *in situ* consolidation can be attained. Disks can be formed from the spherical samples by compression. Such disks are suitable for mechanical tests such as miniaturized disk bend tests or small tensile sample tests.

2.2. Bulk processing methods for severe plastic deformation

The possibility of producing very fine grain size 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 1950's, 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, and strengthening due to cell structures gives an $m = 1$ dependence in the equation $\tau = \tau_0 + kGbd^{-m}$ where τ is the shear flow stress, G the shear modulus, b the Burgers vector, d the cell size, and k and m are constants [30]. Subgrains, like cells, show small misorientations with their neighbors, but have sharper boundaries, and are formed by plastic deformation and thermal recovery processes. The strengthening gives an m value of 0.5, the same as for high angle grain boundaries in

the Hall-Petch equation. 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. However, there have been some reports of severe plastic deformation by multiple pass rolling or drawing that produced nanoscale microstructures [31]. For example, Pavlov has given evidence for the decomposition of the microstructure of Ni, Pt, and several Pt-base alloys first into "fragments" of about 15 nm diameter. The fragment size decreased further with continued deformation and the misorientation between crystallites increased. Eventually, partial amorphization was reported. These results have not been reproduced to the author's knowledge. Rack and Cohen reported [32] the cell structure developed in a series of Fe-Ti alloys 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 microstructures developed, and the properties of the materials with the refined grains so produced have been reviewed by Valiev *et al.* [33].

The major methods reviewed [33] and that have received the most attention from researchers in the field are severe plastic torsion straining under high pressure (SPTS) and equal channel angular pressing (ECAP). In the case of SPTS a disk shaped sample is compressed to pressures of a few GPa and then one of the dies is moved with respect to the other. With enough rotation significant shear strains can be achieved. Even though it would be predicted that the strain distribution might be radial from the disk center, electron microscopy studies have shown approximately uniform microstructures across the disk samples. This is consistent with more detailed calculations that take into account both the compressive and torsional stress states. While in most studies, submicron grain sizes have been produced by SPTS, in some cases nanostructured materials have been prepared. This method has also been successfully used for the consolidation of powders. The ECAP method which allows for the deformation of bulk samples by pure shear was first developed by Segal [34]. 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 to 300 nm, range. A large body of experimental research and modeling studies has been developed for this technique as reviewed by Valiev *et al.* [33] and in subsequent journal articles and conference proceedings. 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 [35].

Another bulk deformation method that has been applied to billet deformation is multiple forging. This was developed by Salischev and co-workers [36]. It involves repeated free forging of a billet with changes of the axis of the applied stress and has been done at elevated temperatures in a variety of Ti, Ni, and Mg- base alloys. The mechanism of grain refinement has been attributed to dynamic recrystallization at the elevated temperatures of processing [33]. For example, Belyakov *et al.* [37] have deformed 304 stainless steel by multiple compressions with the deformation axis changed after every pass to total strains of over 6 at 873K. The formation of the submicron grains observed was attributed to a continuous dynamic recrystallization phenomenon.

Accumulative roll-bonding is a process which can be applied to the grain refinement of sheet samples and in principle scaled up for commercial application to large production quantities of sheet material. The process was first proposed by Saito *et al.* [38] although similar methods had been previously used to prepare nanostructured or amorphous materials by cyclical rolling and stacking of sheets of dissimilar metals [39, 40]. Accumulative roll bonding involves the rolling of a sheet, cutting, cleaning the surfaces, stacking, and rolling the stacked pair to sufficient deformation (typically 50%) to attain good bonding. The process is then repeated and the strain so accumulated can reach large values only dependent on the number of cycles used. While the earlier studies using dissimilar metal sheets, foils, resulted in nanocrystalline or even amorphous structures, the more recent work applied to single phase sheets usually results in submicron rather than nanoscale grain sizes. However, recent work on dissimilar foils also exhibits nanostructured grain formation [e.g. 41]. The number of rolling/stacking cycles in these studies of dissimilar metal composites were large, typically 60-75 times, while the reports of accumulative roll bonding on single composition sheets were

only 7-8 times. Since the total strain is proportional to the number of rolling/stacking cycles, this may explain why nanostructured grains have been obtained in the dissimilar stacked foil experiments and only submicron grains in the single composition studies. Thus, under the appropriate conditions, accumulative roll bonding can be a method to obtain nanostructured microstructures.

Other Bulk Processing Methods that Produce Submicron Grain Sizes. There have been several attempts to design and use alternate techniques for producing refined grain structures by severe plastic deformation. Among these are repetitive corrugation and straightening [42], friction stir welding [43], multipass coin-forging [44], constrained groove pressing [45], and twist extrusion [46]. Repetitive corrugation and straightening involves bending and straightening of sheet samples repetitively to build up significant plastic strain. The advantages cited for this method, which can be adapted to rolling mill technology, are the creation of bulk sheet material with fine grains and free from contamination and porosity [42]. A range of fine grains were observed in Cu subjected to repetitive corrugation and straightening, but the average grain size was submicron, not nanocrystalline. Friction stir welding carried out with the sample cooled to liquid nitrogen temperature, has resulted in submicron grain sizes in aluminum alloys [43]. The mechanism has been attributed to dynamic recrystallization. In multipass coin-forge processing a metal sheet surface is coined between two sine wave shaped dies, with successive rotation of the workpiece, followed by flat forging or rolling. The process is repeated until the deformed surface zones meet. Submicron grain sizes have been obtained. Constrained groove pressing [45] is very similar in principle and results to multipass coin-forging. The concept of twist extrusion – extruding a prismatic billet through a die with a twist channel – has been proposed [46] but no experimental results have been presented.

2.3. Surface deformation methods

It has been known for some time that the microstructures of surfaces subjected to wear processes can be similar to those observed by mechanical attrition; that is nanostructured or submicron grain sizes [8]. Recently K. Lu and co-workers have developed a method to produce controlled severe surface deformation on metallic surfaces [47]. This method is ultrasonic shot peening. Steel balls (3 mm diameter) are vibrated at ultrasonic frequencies and impact the sample surface when resonated by a large number of balls over a short period of time. The surface layers of the sample are severely deformed and nanoscale microstructures are developed in the near surface regions. The refined grains become coarser as the distance from the surface increases. By using TEM the progress of the deformation-induced grain refinement could be followed. This surface mechanical attrition (SMA) technique promises to provide a surface treatment to enhance mechanical and possibly corrosion properties of metals so treated.

Static recrystallization of severely deformed metals. In order for practical production of structural nanostructured materials in industrial operations it would be desired to use conventional deformation processing methods such as rolling, extrusion, or wire drawing followed by appropriate annealing treatments to give microstructures for optimized mechanical behavior. While it has been demonstrated in the past [*e.g.* 32] that severe conventional deformation processes can produce refined microstructures, these microstructures on the nanoscale have been cell or subgrain boundaries. High angle grain boundaries are needed as a substantial percentage of the boundaries to take advantage of the nanocrystalline properties. There have been some recent results that indicate such hoped for processes may be possible.

Wang *et al.* [48] have reported on the preparation and tensile testing of nanostructured/submicron grain sized Cu. They rolled the Cu to 93% at liquid nitrogen temperatures and then annealed it at low temperatures up to 200 °C. The original heavily cold worked Cu had a high dislocation density along with some resolvable grains less than 200 nm in size. Annealing resulted in development of well defined grains with high angle boundaries. The annealing treatment (3 minutes at 200 °C) that optimized strength and ductility produced a mixture of nanoscale/ultra fine grains (80 nm to 200 nm) along with about 25% volume fraction of coarser grains (1 to 3 μm). The coarser grains were the result of secondary recrystallization. The nanoscale grains apparently supplied the strengthening while the larger grains allowed for significant strain hardening which prevents localized deformation and premature fracture. Rolling the Cu at room temperature did not produce the above effects, suggesting that biasing the accumulation of defects (dislocations) versus recovery by thermal processes by rolling at liquid nitrogen was needed to obtain the required deformed structure as a precursor to the development of the fine grained structures on subsequent annealing.

Another example of using conventional thermomechanical processing to obtain a mixture of nanostructured and submicron grain size microstructures was given by Ueji *et al.* [49]. The authors used plain low carbon steels that were austenitized and quenched to produce a martensitic structure. The as-quenched sheets were rolled to a modest strain of 0.8 and then annealed at temperatures of 673K to 973K. The steel annealed about 823K exhibited a microstructure consisting of fine grained ferrite with grain sizes of 50 to 300 nm along with uniformly distributed carbide particles. This material had both high strength (710 MPa yield strength and 870 MPa tensile strength) and good ductility (9% uniform elongation, 20% total elongation). The as-quenched lath martensite in these low carbon steels had a high dislocation density which on subsequent modest plastic deformation by rolling apparently allowed a sufficiently high dislocation density to produce the fine grained microstructure observed. These examples suggest that it should be possible to obtain nanostructured/submicron grain sizes in materials using conventional deformation processing methods combined with annealing in carefully chosen procedures for given materials. An initial high dislocation density appears to be a prerequisite for such behavior.

3. SUMMARY AND CONCLUSIONS

Of the variety of methods discussed in this paper to prepare nanoscale microstructures by severe plastic deformation, only ball milling, high pressure torsion, and accumulative roll bonding appear to be able to regularly produce average grain sizes below 100 nm – that is nanocrystalline materials. Ball milling results in powders which then must be compacted without losing the refined microstructure but with theoretical density and complete particulate bonding. This remains a challenge to this otherwise very versatile method. High pressure torsion is an excellent way to prepare nanocrystalline materials but is limited to small sample sizes. Accumulative roll bonding does not have the limitation of size, but to reach the nanoscale microstructure requires many repetitions which is very labor intensive and may not be a practical industrial process.

However, a few recent examples of combining conventional deformation processing with annealing are encouraging. This suggests that with better understanding of the deformation and recrystallization processes in given materials, thermomechanical methods may be developed that can produce mixtures of nanoscale and submicron grain sizes that can optimize mechanical properties.

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