Processing-Structure-Property Relationships in Ultrafine Grain and Nanocrystalline Materials

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Abstract. This paper will review selected aspects of the processing-structure-property relationships in ultrafine grained (ufg, grain sizes 100 to 500 nm) and nanocrystalline (nc, grain sizes < 100 nm) materials. Of the various processing methods to obtain fine grain size materials, the two that have provided bulk artifact-free samples are electrodeposition and severe plastic deformation. The processing methods and important variables will be described for these techniques. Since the stability of the nanocrystalline microstructure is important for both processing (e.g. consolidation of powders) and elevated temperature mechanical property studies, the stability of nanocrystalline grain sizes as influenced by solute additions will be discussed. While hardness and strength usually increase with decreasing grain size, ductility is typically poor. There are now, however, a number of examples of nanocrystalline materials which combine high strength with good ductility. An example from the author’s laboratory on nanocrystalline Cu with optimized mechanical properties will be presented.

1. Introduction
A common definition of the field of materials science and engineering is the “tetrahedron” of processing-structure-property-performance first expounded by Fleming [1]. Cahn has also stated that “microstructure is the most important single defining theme of MSE (materials science and engineering)”[2]. In the cases of ultrafine grain,(ufg, grain size from 100 to 1000 nm) and nanocrystalline (nc, grain size < 100 nm), materials, the critical microstructural feature that determines properties and performance is the grain size. The grain size, in turn, depends upon the processing method used. A large number of processing methods have been developed for the production of ufg and nc materials. These have been reviewed [e.g. 3] and include inert gas condensation, chemical synthesis of nc powders, electrodeposition, mechanical attrition of powders, chemical and physical vapor deposition of thin films, and severe plastic deformation methods. This paper will concentrate on bulk ufg and nc materials. The properties to be considered are mechanical behavior such as strength and ductility. Since it is now clear that bulk, artifact-free ufg or nc materials are needed for meaningful measurements of mechanical properties, this paper will be confined to those two processing methods that have been shown to produce such materials. These are electrodeposition and severe plastic deformation (including mechanical attrition) methods. This paper will then briefly describe the above two processing methods. The stability of nc grain structures will be discussed since grain size stability is critical for consolidation of powders made by mechanical attrition and for
elevated temperature studies. The paper will conclude with examples of optimized mechanical properties that have been observed in artifact-free nc materials.

2. Electrodeposition as a method to prepare nc materials

Since the late 1980s electrodeposition was studied as a method to prepare nanocrystalline materials and it has moved into the commercial production of such materials. Much of this work was pioneered by Erb and co-workers and this subject has been reviewed by Erb[4]. Electrodeposition is a “one-step” processing method in that the coatings or free-standing foils are nanocrystalline and consolidation of particulates is not required. This eliminates one category of artifact, that is porosity or incomplete particulate bonding, that is common to “two-step” processes. However, other artifacts that can mask inherent behavior of nanocrystalline materials may still be present and will be discussed below.

Electrodeposition occurs by the nucleation of crystallites on the substrate surface and their subsequent growth along with nucleation of new crystallites. In order to have a nanocrystalline grain size, nucleation events should be favored over growth. The variables in electrodeposition include bath composition, bath pH, temperature, overpotential, bath additives, direct current vs. pulse electrodeposition, etc. It has been stated [4] 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 [5]. 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 simply “additives”) on the growing surface. A large number of additives have been identified and used as grain refiners. These are typically organic materials such as saccharin, coumarin, thiorea, and polyacrylamide. The problem with many of these organic additives is that they become trapped at the grain boundaries and are probably responsible for the brittle mechanical behavior observed in nanocrystalline materials processed by electrodeposition with additives. In the co-electrodeposition of alloys, the solute ion can act like an organic additive but without the deleterious embrittlement effects.

The other important process parameter that is critical in controlling the grain size is the overpotential. The overpotential, or “overvoltage” is the deviation of an electrode potential from its equilibrium value required to produce a net flow of current across an electrode / solution interface. Grain growth is favored at low overpotential and high surface diffusion rates while high overpotential and low surface diffusion favor extensive nucleation. A powerful method to achieve high overpotentials is by the use of pulse plating. In this case the peak current density can be much higher than the limiting current density attained for the same electrolyte during direct current plating. In direct current plating only one parameter can be varied, namely, the current density, whereas in pulse electrodeposition there are three parameters which can be varied independently: the peak current density (Jp), the pulse on-time (Ton) and the pulse off-time (Toff). These additional plating parameters make possible the creation of a range of mass transport, eletrocrystallization, and adsorption / desorption situations that are not otherwise possible in direct current plating [6]. In general it has been found that a high peak current density results in smaller grain sizes since the high electrode overpotential greatly increases the free energy available for the formation of new nuclei, resulting in higher nucleation rates and thus smaller crystal size.

While electrodeposition is a one-step process for producing nanocrystalline microstructures, artifacts are possible. Trapped impurities at the grain boundaries from bath additives, if used, can be a source of embrittlement. In some systems high internal stresses can be generated during electrodeposition which can cause cracking [7]. Therefore, while electrodeposition is a powerful method to produce nanocrystalline materials, the processing variables must be optimized to prevent artifacts.

3. Severe plastic deformation to obtain ufg and nc materials
Severe plastic deformation can introduce defects - dislocations and/or twins - which can result in fine grain sizes and/or nanoscale twin bundles. The most common methods for severe plastic deformation are equal channel angular pressing (ECAP), high pressure torsion (HPT), ball milling of powders (and consolidation), and most recently, dynamic plastic deformation at cryogenic temperatures. These methods will be discussed along with their strengths and limitations.

3.1 Equal channel angular pressing - ECAP
The ECAP method which allows for the deformation of bulk samples by pure shear was first developed by Segal et al. [8]. 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. [9] 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.

3.2 High pressure torsion - HPT
In HPT a disk shaped sample is compressed to pressures of about 2 to 6 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 relatively uniform microstructures across the disk samples in some cases. 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 HPT, in some cases nanostructured materials have been prepared. This method has also been successfully used for the consolidation of powders.

3.4 Ball milling and consolidation of powders
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, [9,10].

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 upon a number of variables as well as properties of the element, alloy, or compound being milled. The minimum grain size obtainable by milling, \( d_{\text{min}} \), has been attributed to a balance between the defect/dislocation structure introduced by the plastic deformation of milling and its recovery by thermal processes [11]. 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 [11].

The mechanisms for the formation of nanocrystalline microstructures by mechanical attrition were first proposed by Fecht et al, [12]. This explanation was based upon the TEM studies of ball milled Ru and AlRu powders. 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 cells / 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 by mechanical milling. However, from the results on cryomilled Zn [13] 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.

While ball milling of powders is usually a two-step process which requires a powder consolidation step, a recent ball-milling strategy has been developed that provides for in situ powder consolidation during milling [14]. This is accomplished by a judicious selection of milling temperatures (liquid-nitrogen and room temperature combinations), milling times at each temperature, and ball/powder mass ratios. In certain ductile metals it is found that solid spheres up to 10-15 mm in diameter can be formed. These can then be pressed into disks for a variety of mechanical tests. Metals and alloys that have been processed in this way include Zn, Cu, Al, and several Cu and Al alloys.

3.5 Dynamic plastic deformation - DPD
A recent method of severe plastic deformation to create nanocrystalline microstructures was developed by Lu and co-workers [15]. This technique uses plastic deformation at high compressive strain rates by dynamic loading at strain rates about $10^2 - 10^3$ s$^{-1}$. The use of DPD at liquid nitrogen temperature on Cu samples resulted in the formation of a high density of mechanical nano-scale twins along with a high dislocation density. This structure led to good mechanical properties such that a tensile yield strength of 600 MPa and an elongation-to-failure of 11% were observed.

4. Stability of nanocrystalline grain structures

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. Understanding the scientific nature of stability, grain growth of nanocrystalline microstructures, is a criterion for allowing strategies to 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 [16], Weissmuller [17], and Malow and Koch [18].

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 multi-component, 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 [19], second phase drag [20], solute drag [21], and chemical ordering [22]. 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 [23,24], Kirchheim [25], Liu and Kirchheim [26], and Millett et al.[27]. 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 \( \text{Pd}_{100-x}\text{Zr}_x \) alloys [26]. 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.

Recently, Darling et al. [28] studied the influence of solute Zr atoms on the stability of the grain size of nanocrystalline Fe. Zr was selected for this study of potential thermodynamic stabilization because Zr in Fe has a large positive elastic enthalpy of \(+92 \text{ kJ/mol}\) and a large negative enthalpy of mixing of \(-118 \text{ kJ/mol}\) [29]. The large elastic enthalpy indicates that these alloys should favor grain boundary segregation of solute atoms. These thermodynamic data suggest that nanocrystalline Fe(Zr) should be an ideal system for a study of thermodynamic grain size stabilization. The nanocrystalline Fe(Zr) alloys were prepared by ball milling of the elemental powders at compositions of 1, 4, 7, and 10 atomic percent Zr. Milling was carried out for 20 hours at room temperature. The milled powders, after characterization for grain size, were subsequently heat treated at 340, 500, 700, 850, 1000, 1150, and 1375 °C for 60 minutes in an Ar/2%H\(_2\) atmosphere. The as-milled powders showed metastable solid solubility for all the alloys (1-10 at. % Zr) studied. On annealing, precipitation of \( \text{Fe}_2\text{Zr} \) was observed at 1000°C for the 7 at. % Zr alloy, and at 500°C for the 10 at. % Zr alloy. The 1 and 4 at. %Zr alloys maintained complete solubility (from x-ray diffraction measurements) at all annealing temperatures and times including 1375°C for one hour. On isothermal annealing it was found that the grain size grew initially, and then stagnated with further annealing time. At the same time the lattice parameter of the Fe (Zr) solid solution decreased rapidly toward that of pure Fe. The drop in lattice parameter on annealing must mean that Zr solute atoms leave the Fe lattice and segregate to the grain boundaries. However, energy dispersive spectroscopy (EDS) showed that some Zr segregation to the particle surfaces also occurred. Therefore, a precise analysis of the amount of Zr segregated to the grain boundaries was not possible. The grain size versus \( T/T_M \), where \( T \) is the annealing temperature, and \( T_M \) is the liquidus temperature of the alloy, is given in Fig. 1 for nanocrystalline Fe, Fe-10 at. % Cr, Fe-1 at. % Zr, and Fe-4 at. % Zr.

![Grain size versus reduced annealing temperature (T/T_M) for Fe](image)

Grain size versus reduced annealing temperature (T/T\(_M\)) for Fe ●
Fe-10 wt. % Cr ○; Fe-1 at. % Zr ▼; Fe-4 at. % Zr ▽ [30].
It is evident that the grain size of pure nanocrystalline Fe grows to greater than 100 nm at temperatures below about 0.5 T/\text{TM}. The addition of 10 wt. \% Cr to nanocrystalline Fe has little effect of the grain size stabilization, as might be expected since Cr has a similar atomic size to Fe and the elastic enthalpy is \approx 0 such that complete solubility is observed and little grain boundary segregation is likely. However, both the 1 and 4 at. \% Zr additions to nanocrystalline Fe resulted in significant stabilization of the grains with little difference between the 1 and 4 at. \% Zr alloys. There is very little grain growth in the Fe-1 at. \%Zr nanocrystalline alloy until about 0.5 T/\text{TM}. However, this grain growth stops at a temperature between 0.6 and 0.7 T/\text{TM}, and remarkably, stays about constant up to temperatures near the melting point, i.e. 92-95% of T_{\text{M}}. Based on a simple estimate, and the observation of surface segregation and lattice parameter change in the Fe-1 at. \% Zr alloy, it appears that stabilization can be achieved with less than a monolayer of Zr on the grain boundaries. Increasing the solute content to 4 at.\% Zr produced no additional stabilization and no intermediate phases.

5. Optimized mechanical behavior for nanocrystalline materials.

While it has been known for many years that nanostructured metals can have hardness and strength values much higher than conventional grain size counterparts, ductility has been disappointingly low. Most nanocrystalline materials with grain size less than about 30 nm showed little ductility in tension, typically less than 2 \% elongation to failure. However, as reported in a review of this topic [31], there are now several examples of nanostructured metals and alloys that exhibit optimized values of both high strength along with good ductility. The removal of possible artifacts that can mask inherent behavior are clearly important in both the examples of electrodeposited and ball milled and in situ consolidated materials. Whether this is the main reason for the observed behavior is still not evident. The appearance of significant strain hardening in the samples that show optimized strength and ductility needs further study.

An example of a nanocrystalline material that exhibits both high strength and ductility is nanocrystalline Cu made by \textit{in situ} consolidation ball milling as briefly described in section 3. Bulk nanocrystalline Cu spheres were synthesized using a combination of liquid nitrogen temperature and room temperature milling [32]. 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 2A 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 2A. Statistical analysis of multiple dark field images reveals a monotonic lognormal grain size distribution with an average grain size of 23 nm (Figure 2B).

Figure 2. A; bright field micrograph of nanocrystalline Cu, B distribution of grain size from dark field.
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 3 [33]. In the case of the nanocrystalline Cu, the 0.2 % offset yield strength ($\sigma_y$) and the ultimate tensile strength ($\sigma_u$) reach values of 971 + 12 MPa and 1120 + 29 MPa respectively. This $\sigma_y$ value is at least one order of magnitude higher than that of coarse-grained pure Cu samples, and $\sigma_u$ of the nanocrystalline Cu is about five times higher than that of the coarse-grained Cu sample. 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. Another important feature of the stress-strain curve (Figure 3) 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.

![Figure 3. Stress-strain curves for in situ consolidated bulk nanocrystalline Cu compared to conventional grain size Cu, and to nanocrystalline Cu made by the inert-gas condensation and compaction method. [33]](image)

6. Summary

This paper has given a brief description of the importance of processing-structure-property relationships for selected examples of nanocrystalline materials prepared by electrodeposition and severe plastic deformation methods. The stability of nanocrystalline microstructures as controlled by solute additions was also addressed. An example of a nanocrystalline material that has both high strength and good ductility was presented.
References
[1] Flemings, M. C. 1999 Annu. Rev. Mater. Sci. 29 1
[2] Cahn, R. W. 2001 The Coming of Materials Science, Pergamon, Amsterdam, p.539.
[3] Koch, C. C., Ovid’ko, I. A., Seal, S., and Veprek, S. 2007 Structural Nanocrystalline Materials, Cambridge University Press, Chapter 2.
[4] Erb, U., Aust, K. T., and Palumbo, 2007 G. Electrodeposited Nanocrystalline Metals, Alloys, and Composites, in Nanostructured Materials, ed. C. C. Koch, William Andrew, pp.235-283.
[5] Bockris, J. O. M. and Razumney, G. A. 1967 Fundamental Aspects of Electrocrystallization, Plenum Press, NY, p. 27.
[6] Pupipe, J. Cl. 1986 in Theory and Practice of Pulse Plating, ed. Pupipe, J. Cl., and Leaman, F., Orlando FL: AESF, p.1.
[7] Li, H. and Ebrahim, F. 2003 Mater. Sci. Engr. A, 347, 93
[8] Segal, V. M., Reznikov, V. I., Drobyshvkiy, A. E., and Kopylov, V. I., 1981 Metally, 1, 115.
[9] Koch, C. C. 1991, in Materials Science and Technology, ed. Cahn, R. W., Haasen, P. and Kramer, E. J. vol. 15. VCH, Weinheim, p. 193.
[10] Suryanarayana, C. 2004, Mechanical Alloying and Milling, Marcel Dekker, NY.
[11] Eckert, J. Holzer, J. C., Krill, C. E., and Johnson, W. L. 1992, J. Mater. Res., 7, 1751.
[12] Fecht, H J., Hellstern, E., Fu, Z., and Johnson, W. L. 1990, Metall. Trans. A, 21A, 2333.
[13] Zhang, X., Wang, H., Scattogood, R. O., Narayan, J., and Koch, C. C., 2002, Acta Mater., 50, 3935.
[14] Zhu, X. K., Zhang, X., Wang, H., Sergueeva, A. V., Mukherjee, A. K., Scattogood, R. O., Narayana, J., and Koch, C. C. 2003, Scripta Mater., 49, 429.
[15] Zhao, W. S., Tao, N. R., Guo, J. Y., Lu, Q. H., and Lu, K., 2005, Scripta Mater. 53, 745.
[16] Suryanarayana, C. 1995, Intl. Mater. Rev. 40, 41.
[17] Weismuller, J. in Synthesis and Processing of Nanocrystalline Powder, ed. Bourell, D. L., TMS, Warrendale, PA, 1996, p. 3.
[18] Malow, T. R. and Koch, C. C. in Synthesis and Processing of Nanocrystalline Powder, ed. Bourell, D. L., TMS, Warrendale, PA, 1996, p. 33.
[19] Hofler, H. J., and Averback, R. S., 1990, Scripta Metall. Mater. 24, 2401.
[20] Boylan, K., Osstrander, D., Erb, U., Palumbo, G., and Aust, K. T., 1991,Scripta Metall. Mater. 25, 2711.
[21] Michels, A., Krill, C. E., Ihrhardt, H., Birringer, R., and Wu, D. T., 1999, Acta Mater. 47, 2143.
[22] Gao, Z. and Fultz, B., 1994, NanoStructured Mater. 4, 939.
[23] Weismuller, J., 1993, NanoStructured Mater. 3, 261.
[24] Weismuller, J., 1994, J. Mater. Res. 9, 4.
[25] Kirchheim, R., 2002, Acta Mater. 50, 413.
[26] Liu, F. and Kirchheim, R., 2004, Scripta Mater. 51, 521.
[27] Millett, P. C., Selvam, R. P., and Saxena, A., 2007, Acta Mater. 55, 2329.
[28] Darling, K. A., Chan, R. N., Wong, P. Z., Semones, J. E., Scattogood, R. O., and Koch, C. C., 2008, Scripta Mater., in press.
[29] De Boer, P. R., Boom, R., Mattens, W. C. M., Miedema, A. R., and Niessen, A. K., 1988, Cohesion in Metals: Transition Metal Alloys, North-Holland, Amsterdam, p. 748.
[30] Koch, C. C., Scattogood, R. O., Darling, K. A., and Semones, J. E., 2008, J. Mater. Sci., in press
[31] Koch, C. C., Youssef, K. M., Scattogood, R. O., and Murty, K. L., 2005, Advanced Engr. Mater. 7, 787.
[32] Youssef, K. M., Scattogood, R. O., Murty, K. L., and Koch, C. C., 2004, Appl. Phys. Lett., 84, 929.
[33] Youssef, K. M., Scattogood, R. O., Murty, K. L., Horton, J. A., and Koch, C. C., 2005, Appl. Phys. Lett., 87, 091904-1-3.