

Chapter 2

Nanostructured Materials

Abstract A general description of nanocrystalline materials is given. The conditions for obtaining a nanostructure are briefly discussed. Measurement of the crystallite size and microstrain by Rietveld method is explained.

Keywords Crystallite size • Rietveld refinement

2.1 General Considerations

There are many ways to synthesize nanocrystalline and/or nanocomposite materials. One way to class them is by the material's phase during synthesis [1]. From the vapor phase, techniques such as physical vapor deposition, chemical vapor deposition, and aerosol spraying could be used. The liquid route involves sol–gel and wet chemical methods. In the case of solid state route, the privileged way is mechanical milling and mechanochemical synthesis. Each method has its own advantages and shortcomings. Among these techniques, mechanical milling and spray conversion processing are commonly used to produce large quantities of nanopowders [1]. The advantage of using mechanical milling for the synthesis of nanocrystalline materials lies in its ability to produce bulk quantities of material in the solid state using simple equipment and at room temperature.

The unique properties of nanocrystalline materials are derived from the relative importance of grain boundaries compared to their coarse-grained polycrystalline counterparts. For most metals and alloys, a grain size refinement down to nanometer scale results in considerable growth of strength and hardness [2].

Assuming that the grains have a spherical shape and that the grain boundary thickness is much smaller than the grain radius, the relative volume of grain boundaries and grain is approximately given by:

$$\frac{V_{GB}}{V_G} \cong 3 \frac{t_{GB}}{r_G}, \quad (2.1)$$

where t_{GB} is the grain boundary thickness, r_G is the grain radius, and V_{GB} , V_B are respectively the volume of grain boundaries and grains. From this equation, one can see that for a grain boundary of 1 nm thickness and particles of 10 nm radius about 30 % of the material is in the grain boundaries. Thus the interface structure plays an important role in determining the physical and mechanical properties of nanocrystalline materials.

The minimum grain size achievable by milling is determined by the competition between the plastic deformation via dislocation motion and the recovery and recrystallization behavior of the material. It was found that for Al, Ag, Cu, and Ni (all of which having an fcc structure) there is an inverse dependence of minimum grain size on the melting point [3]. However, the minimum grain size is virtually independent of the melting point for the hcp, bcc, and other fcc metals with high melting points. In this case, it appears that the grain size is in the order: fcc < bcc < hcp [3]. However, process variables (milling intensity, milling temperature, alloying effects, contamination, etc.) can influence the minimum grain size achieved.

2.2 Measurement of Crystallite Size

In many cases, crystallite size is determined from X-ray powder diffraction peak broadening. This is a fast and efficient way to measure crystallite size but some care should be exerted. First, peak broadening is due to crystallite size but also to microstrain. A number of methods exist to distinguish these two effects. Historically, methods such as Williamson-Hall (W-H) or Warren-Averbach have been extensively used. These two methods are based on a Line Profile Analysis (LPA) where each Bragg peak is analyzed individually. Unfortunately, these methods could not be reliably used in the presence of complex background and peak overlap [4]. With the advent of computing power and freely available softwares, more powerful methods of analysis are now available.

The most powerful method is the Rietveld refinement in which the whole diffraction pattern is fitted at once and crystal structure parameters are refined. Usually these parameters are: background, atomic positions, disorder or mixing between atomic sites, thermal, lattice, peak shape, preferred orientation, etc. From the peak shape parameters, the crystallite size and strain could be extracted [5]. This method is very powerful and is extensively used. More details about this method could be found in Refs. [6, 7].

One disadvantage of Rietveld method is that it requires a priori knowledge of the material's crystal structure. When such information is not available, usage of the whole pattern is still possible by using the so-called whole powder pattern decomposition (WPPD) methods. Here, two variants exist: the Pawley and the LeBail methods. In the Pawley method, peaks intensities are considered as refinable parameters contrary to Rietveld method where intensities are derived from the structure. For overlapping peaks correlation is reduced by introducing both constraints and restraints into the least-squares procedure. This makes the refinement

quite time consuming and impractical. In the LeBail method these problems are solved by not refining the intensities of the individual peaks. This considerably reduces the number of parameters to fit in the least-square program. Moreover, LeBail code is easier to implement into existing Rietveld programs. Both Pawley and LeBail methods as well as Rietveld refinement are now available in freeware and commercial programs [8]. As they are much more powerful and reliable than conventional W-H and Fourier methods, it is recommended to use them for crystallite size and microstrain evaluation.

In the determination of crystallite size and microstrain, irrespective of the method used (W-H, Rietveld, WPPD), the contribution from the instrument should be subtracted. Until recently, this was made by running a reference standard with large crystallite (polycrystalline) and no microstrain. Bragg peaks are then fitted by using simple analytical functions such as Voight, pseudo-Voight, or Pearson VII to get the instrumental profile parameters. These parameters are then used in the deconvolution process of the sample pattern in order to extract the crystallite size and microstrain. An alternative to this procedure is the use of so-called *Fundamental Parameters* approach [9]. In this method, the instrument geometry is used to calculate the instrument profile thus eliminating the need to measure a reference standard. As long as the instrument geometry is well defined, this method seems to be more reliable than the one using a standard reference.

Finally, another effect to take into account is the presence of stacking faults. In the presence of stacking faults, the effective crystallite size (D_{eff}) is given from peak broadening due to contribution from the true average crystallite size (D_{true}) and the effective stacking fault diameter (D_{SF}) according to the relation [4]:

$$\frac{1}{D_{\text{eff}}} = \frac{1}{D_{\text{true}}} + \frac{1}{D_{\text{SF}}}, \quad (2.2)$$

Thus, if it is assumed that the peak broadening is only due to the small crystallite size, then the calculated crystallite size grossly underestimates the true crystallite size. For the mechanically alloyed Cu–Co alloys it has been shown that the true crystallite size was 3–10 times the apparent crystallite size [10]. The contribution of stacking faults to broadening/shift of peak positions is very important in alloys with low to moderate stacking fault energy, where a high density of stacking faults can be expected [3].

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Enhancing Hydrogen Storage Properties of Metal
Hybrides

Enhancement by Mechanical Deformations

Huot, J.

2016, VI, 39 p. 14 illus., 6 illus. in color., Softcover

ISBN: 978-3-319-35106-3