Chapter 1. Introduction

Nanomaterials, solids with sizes of their building blocks smaller than 100 nm [Gle 2003 and Sur 2000], are an attractive class of materials due to their stimulating properties. Despite having the same chemical composition of their polycrystalline counterparts, nanomaterials generally display a significant improvement of the properties. This is ascribed to their small grain/crystallite sizes and to the resulting effects on the deformation mechanism: the critical length scale and the volume fraction of grain-boundaries. Each phenomenon corresponding to a certain property comprises a critical length scale [Sie 1993]. If the grain/crystallite size of the material is smaller than a certain length scale, the corresponding property will be strongly affected [Sie 1993]. As a typical example, small grain sizes result in a shorter distance between the pinning points of a Frank-Read source, leading to a higher force required for the generation of new dislocations. This leads to a considerable increase of the strength of nanostructured materials. Small grain/crystallite sizes lead to a large volume fraction of grain-boundary areas (Fig. 1.1). For example, the volume fractions of grain-boundaries are 3, 30, and 50 % for materials with grain sizes of 100, 10, and 5 nm, respectively [Mey 2006]. As the grain-boundaries comprise different properties compared to the bulk of the crystal, the overall properties of the solid is consequently affected.

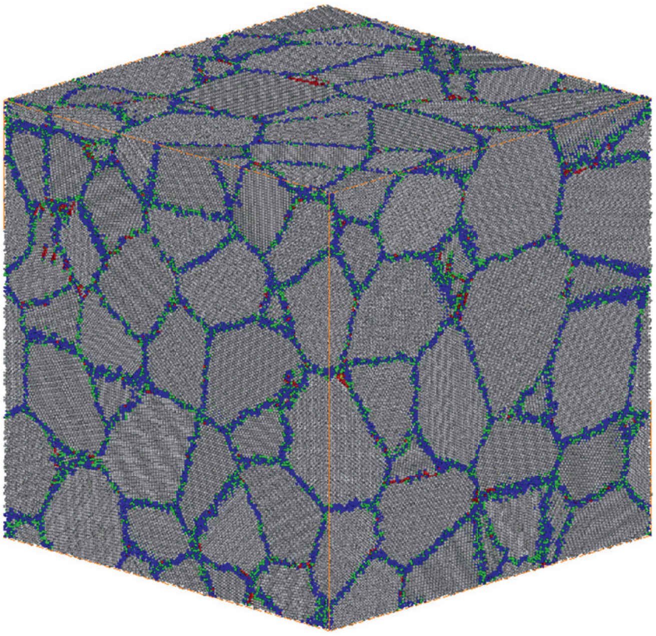

Figure 1.1, schematic representation of a nanostructured material [Swy 2002].

Another important factor that has a strong influence on the properties of a nanostructured material is the method of production [Gle 1995]. Different processing routes have been used to synthesize nanostructured materials. Each of the processing methods leads to some differences in the microstructure of the nanocrystalline phases despite having the same composition and even the same grain/crystallite size. For example, the structure of the grain-boundaries is different in nanomaterials produced by electrodeposition with respect to the corresponding nanophases processed by methods based on severe plastic deformation (SPD). The grain-boundaries of SPD-processed nanomaterials comprise stronger strain fields and, consequently, an excess free energy compared to nanostructured materials produced by electrodeposition. As a result, nanomaterials processed by different techniques may exhibit dissimilar properties.

The way nanostructures are formed or, more precisely, the mechanism of nanostructure formation, can be very different even for a given method of production. For example, nanostructures may be produced during ball milling through partitioning of initial large grains, i.e. through *structural decomposition* [Fec 1995 and Koc 1997], or they can be generated through nucleation and growth of new grains, i.e. by *dynamic recrystallization* [Zha 2001 and Zha 2002[b]]. The inherent properties of the materials can also affect the mechanism of nanostructure formation. The stacking-fault energy (SFE) is a factor that can significantly influence the mechanism of grain refinement. This is because the variation of the SFE influences the dislocation structure and the recovery process [Uek 1987].

This thesis deals with these issues experimentally by clarifying the effect of the SFE on the mechanism of nanostructure formation during ball milling at cryogenic temperature (i.e. cryomilling). For that, structural analysis and the characterization of the lattice defects during cryomilling have been investigated for pure Cu, and Cu-Al and Cu-Zn alloys using different analytical techniques, including X-ray diffraction (XRD), scanning (SEM) and transmission (TEM) electron microscopy. These materials were selected because the addition of Al and Zn to Cu is known to decrease the SFE [Fre 2010].

The thesis is structured as follows: Chapter 2 introduces the different types of nanostructured materials, the methods used for their preparation and the different aspects characterizing their structure. Details on the thermal stability of nanostructured phases and their consolidation are discussed along with the physical and mechanical properties of these fascinating materials. Finally, a brief summary of the deformation behavior is given in the final part of Chapter 2. Details about sample preparation and characterization methods used in the present thesis are presented in Chapter 3.

In Chapter 4, the results obtained by XRD, SEM and TEM, the most commonly used tools for the characterization of nanostructured materials, are critically discussed, with specific focus on the evaluation of the grain/crystallite size. Chapter 5 presents a comprehensive investigation of the mechanisms of nanostructure formation during cryomilling of Cu-based alloys as a function of the SFE. This includes the quantification of the different types of lattice defects and their evolution during cryomilling by XRD analysis combined with the detailed investigation of the defected microstructure by TEM. The thermal stability of the nanocrystalline powders, which is a crucial aspect for retaining the nanostructure during powder consolidation, and the evolution of the lattice defects as a function of temperature is reported in Chapter 6 along with the mechanisms responsible for the grain coarsening. Finally, the conclusions drawn from this work are given in Chapter 7.

Chapter 2. Theoretical background

2.1 Nanostructured materials

Nanostructured materials [Gle 2003 and Sur 2000] are defined as materials with grain sizes less than 100 nm. Above this size value and below 1000 nm they are generally termed ultrafine-grained materials. The border of 100 nm originates from the dramatic change that occurs in the properties of a solid when its building blocks are smaller than this value [Sie 1993]. Confinement effects are responsible for this behavior. In fact, a property will be altered once an entity or mechanism responsible for that property is confined within a size range which is smaller than a critical length scale [Sie 1993]. Furthermore, the volume fraction of grain-boundaries becomes considerable for materials with grain sizes smaller than 100 nm [Gle 1992[a], Gle 2003, and Sur 2000]. This can be clearly seen in Fig. 2.1, which schematically illustrates the atomic structure of a nanostructured material. As grain-boundaries comprise different atomic structure and atomic density and thus different properties compared to the bulk of the crystal [Gle 2003], the overall properties of nanostructured materials progressively diverge from those characterizing their polycrystalline counterparts with increasing volume fraction of grain-boundaries (i.e. with decreasing the grain size).

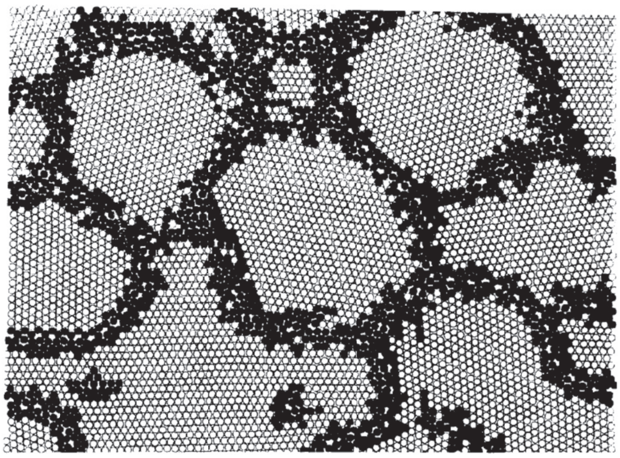

Figure 2.1, schematic view of the atomic structure of nanocrystalline materials [Gle 1995].

In general, a considerable improvement of the properties is achieved due to nanostructure formation [Sur 2000], which makes this class of materials very attractive for a wide range of applications. For example, nanostructured materials comprise higher strength, hardness, and toughness in comparison to their polycrystalline counterparts [Hal

1951, Mey 2006, and Pet 1953]. Furthermore, they exhibit enhanced diffusivity, larger thermal expansion coefficient, higher specific heat and improved soft magnetic properties [Mey 2006 and Wür 2003]. However, they generally display limited plastic deformation [Mey 2006], which severely limits their applications as engineering materials.

2.1.1 Categorization of nanostructured materials

Glieter [Gle 2003] classified non-polymeric nanostructured materials according to their chemical composition and the shape of the microstructural constituents (Fig. 2.2). Considering only the shape, nanostructured materials can be categorized into three main groups: layer-shaped crystallites (thickness in the nanometer range), rod-shaped crystallites (diameter in the nanometer range), and nanostructured materials comprising equiaxed nanocrystals. Additionally, these three groups can be further classified into four families according to their chemical composition as follows [Gle 2003]:

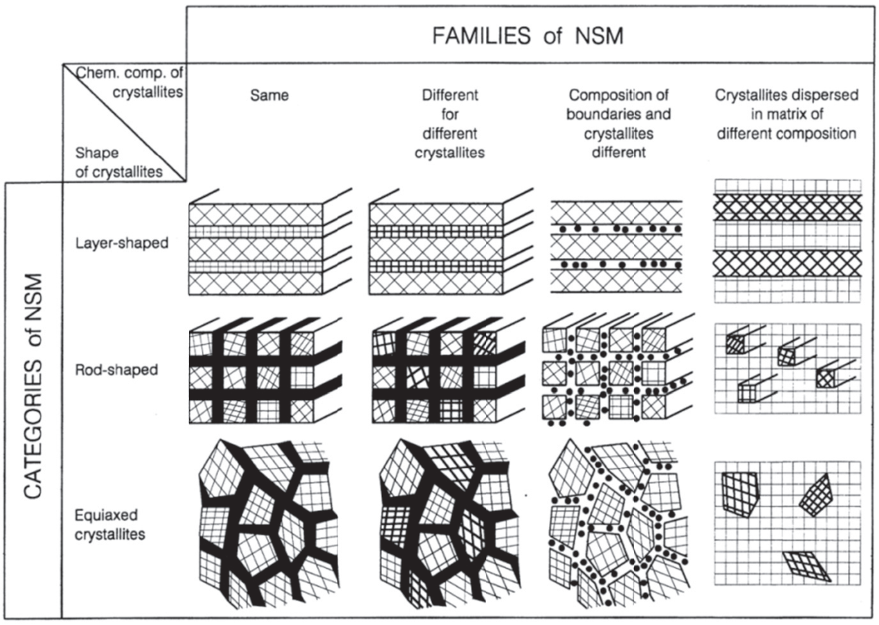

Figure 2.2, classification of nanostructured materials according to their shape and chemical composition [Gle 2003].

1- All crystallites and interfacial regions have the same composition. Semicrystalline polymers composed of stacked crystalline lamellae separated by non-crystalline regions are examples of such structures that belong to the first category. Another example is a nanostructured material composed of equiaxed nanometer-sized crystals, like nanostructured Cu. This belongs to the third category [Gle 2003].

2- Nanostructured materials consisting of crystallites with different chemical composition. Example of such structures are quantum well (multilayer) structures [Gle 2003].

3- The chemical composition of crystallites and interfacial regions are different. In these structures, one type of atoms segregates to the boundary regions. Nanostructured W with segregated Ga atoms at grain-boundaries is an example of such materials (third category) [Gle 2003].

4- Nanometer-sized crystallites, including layers, rods or equiaxed nanocrystals that are dispersed into a matrix with a different chemical composition. Materials obtained by precipitation hardening, in which the size of precipitates is in the nanometer range, belong to this group [Gle 2003].

2.2 Synthesis of nanostructured materials

Nanostructured materials can be synthesized using a variety of different methods. It is important to mention that the properties of nanostructured materials strongly depend on the method of production as well as on their thermal history [Gle 1995]. In general, the processing routes for the production of nanostructures can be divided into two main categories: (a) bottom-up and (b) top-down processes.

In bottom-up processes, nanostructures are obtained from their atomic and molecular constituents through self-organized growth. Inert-gas condensation [Gle 1989 and Sur 2000], sol-gel processing [Mac 2007], devitrification of amorphous phase [Lu 1996, Sur 2000, and Yos 1988], chemical vapor deposition (CVD) [Sta 2009, Wei 2010], plasma or flame spraying synthesis [Fen 2008], laser pyrolysis [Jia 2010], electrochemical processes [Che 1994[a], Gom 1997, Yos 1998, Mat 2004, Wan 2005, Ish 2011] and atomic or molecular condensation [Xia 2004] are different types of bottom-up processes. Among these techniques, the deposition methods (e.g. electrodeposition) have been used extensively to produce nanostructured stripes that can be tested mechanically in tension [Lu 2004, Zha 2004a, Zha 2004[b], Han 2005[c], She 2005, Tao 2006, Liu 2009]. The main limitation of this method is the small thickness of the deposited nanostructures.

The second group of production methods, i.e. nanostructure formation by the top-down approach, is based on the structural decomposition of coarse-grained materials. Within this group, methods based on severe plastic deformation (SPD) are the most used. The main advantage of SPD is that, through this method, in most cases the dimensions of the bulk nanocrystalline specimens are preserved. Some of the important processes based on severe plastic deformation include: high pressure torsion (HPT) [San 2011], equal-channel angular pressing/extrusion (ECAP/ECAE) [Zhu 2003], multiple forging [Gou 2007, Zha 2009], accumulative roll bonding (ARB) [Sai 1999], repetitive corrugation and straightening [Hua 2001, Hua 2004], friction stir welding (friction stir process) [Hu 2008, Kwo 2003[a], Kwo 2003[b], Lee 2006,], continuous confined strip shearing (C2S2) [Huh 2004, Kan 2008], twist extrusion [Ber 2007, Bey, 2009, Var 2008], cyclic extrusion compression [Ric 1999, Ric 2005], and ball milling (BM) [Koc 1997]. Although the nanostructured products obtained by ball milling are in powder form, BM is considered an SPD-based method because the powder particles undergo considerable plastic deformation during processing.

The most important features of selected bottom-up and top-down processes for the synthesis of nanostructured materials are summarized in the following.

- *Electrodeposition*:

In this process, thin layers of a material are deposited from an electrolyte on a substrate by the application of an electrical potential [Erb 1995 and Sur 2000]. The process variables during electrodeposition (e.g. composition of the electrolyte, current density, pH, and temperature of the bath) can be adjusted in order to produce artifact-free nanostructures [Erb 1995 and Sur 2000]. For that, the electrodeposition conditions should be selected in such a way that nucleation is favored over grain growth [Sur 2000].

- *Inert gas condensation*:

In this method, a metal is firstly evaporated inside a chamber. The atmosphere of the chamber is cleaned before the initiation of the process by evacuating to very high vacuum followed by filling the chamber with an inert gas [Gle 1989, Gra 1976, and Sur 2000]. The pressure of the inert gas is typically in the order of a few hundreds Pascals. The evaporated metal atoms lose their kinetic energy by the collision with the inert gas atoms and, therefore, condense to form individual crystals with size of a few nanometers [Sie 1993, Sur 2000]. The fine nanocrystalline powder is then gathered into a collector device from where it is transferred to a compaction unit to form a consolidated nanocrystalline bulk. The compaction is generally done in two stages [Gle 1992[a]]. In the first stage, a green compact is produced by applying low pressures. The green compact is then moved to a high pressure unit in which final compaction is accomplished [Gle 1992[a]]. Powder handling, transfer, and consolidation are carried out under ultra-high vacuum to avoid trapping of gas atoms within the consolidated bulk [Gle 1992[a], Sie 1990, and Sur 2000].

- *Devitrification of amorphous phases*:

This method is based on the crystallization of an amorphous phase [Lu 1996 and Yos 1988]. Different methods are used to obtain the initial amorphous material. Rapid solidification from the molten state, ball milling, vapor deposition, and electro deposition are examples of these methods. However, rapid solidification from the liquid state is generally preferred as it can provide relatively large specimens [Sur 2000]. The crystallization of the amorphous phase has to be controlled precisely in order to promote high nucleation rates and low growth rates [Lu 1996, Yos 1988]. Consequently, a nanocrystalline material is obtained after crystallization. Porosity-free samples can be synthesized using this method. It is also capable of producing large amounts of nanocrystalline samples with different grain sizes. This is achieved by controlling the crystallization conditions [Lu 1996, Sur 1995, and Yos 1988].

- *Equal-channel angular pressing* (*ECAP)*:

In this process, a billet is forced to pass through a die that contains two channels [Mey 2006 and Val 2000]. These channels have the same cross-section but different orientation (see Fig. 2.3). The amount of deformation depends on two factors: (1) the angle between the channels, φ, and (2) the angle of the outer arc of the curvature, ψ [Mey 2006]. The advantage of this method is that the sample can be repeatedly pressed through the die as the dimensions of the cross-section of the sample are preserved. This makes it possible to apply large amounts of strain using this technique. The grain size of materials processed using ECAP is generally in the ultrafine-grained regime. However, grain sizes down to 50 nm have been obtained for large numbers of passes [Mey 2006].

- *Ball milling*:

Ball milling is a versatile process that is capable of producing nanostructures in a wide range of chemical composition and crystal structures [Fec 2002]. In this process, the raw materials in the form of powders are charged into a container (i.e. the milling vial) together with the milling media (generally stainless steel or tungsten-carbide balls). The impact energy of the milling balls is the tool to convert raw materials to products [Jan 2005, Sur 2001] (Fig. 2.4). Ball milling can be divided into two different categories depending on the starting material used [Jan 2005]. The term “mechanical alloying” is used when a chemical reaction or alloying occurs during the ball milling process. On the other hand, the process is called “mechanical milling” when the purpose of milling is to modify the structure or to induce phase transformation in single-phase materials [Jan 2005].

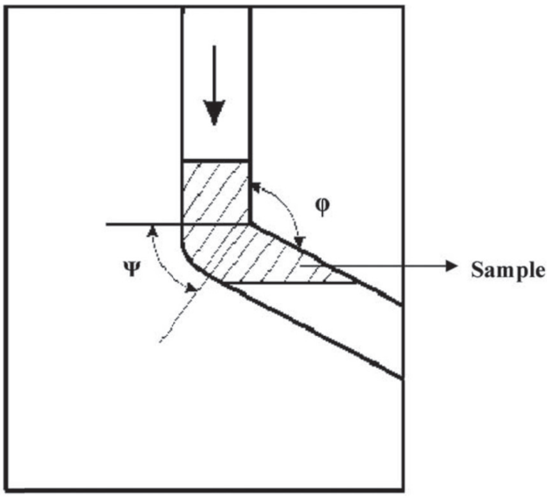

Fig. 2.3, schematic representation of ECAP.

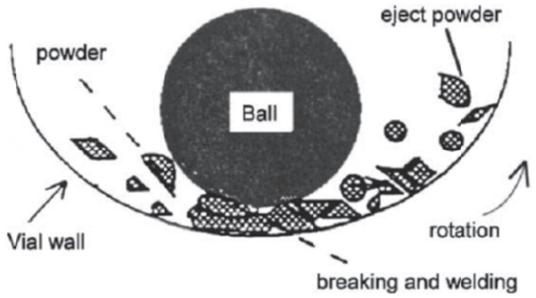

Figure 2.4, schematic illustration of the ball milling process [Jan 2005].

Different types of mills can be used for ball milling. Planetary ball mills or SPEX shaker mills are the most common types of laboratory mills. Planetary ball mills are used in this work in order to prepare nanostructured Cu-based alloys. The term “planetary” originates from the planet type movement of the vials [Sur 2001]. A schematic representation of a planetary ball mill is shown in Fig. 2.5. The vials are placed on a tray rotating with rotation speed Ω, while the vials are rotating in the opposite direction with rotation speed ω [Jan 2005]. The centrifugal forces resulting from the rotation of vials and tray act on the milling charge (balls and powders), imparting two types of movement on the milling balls: (a) running down of the milling balls on the vials, the friction effect, and

(b) free movement of the balls from one side toward the opposite wall, the impact effect [Sur 2001]. The amount of friction or the impact modes depend on the ratio between ω and Ω [Jan 2005]. According to Le Brun et al. [LeB 1993], if the ratio of ω/Ω is small, the balls are immediately pushed back after hitting the opposite wall. This mode is called chaotic. On the other hand, at high ratios of ω/Ω, the balls mostly slide on the wall of the vials and the milling regime is called frictional mode. At the intermediate ratios of ω/Ω, both of the frictional and chaotic modes coexist [Jan 2005 and LeB 1993].

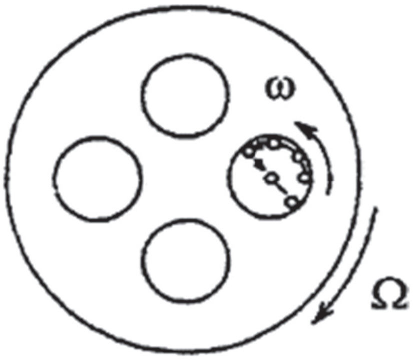

Figure 2.5, schematic representation of a planetary ball mill [Jan 2005].

The milling process depends on a variety of parameters, including ball-to-powder weight ratio (BPR), rotational speed, milling time, size and size distribution of the milling balls, filling rate, and milling temperature [Jan 2005, Sur 2001]. In the following, the effects of these parameters on the milling process are briefly discussed.

- *Ball-to-powder weight ratio (BPR)*: In general, for a given milling-induced phase transformation, the higher is the BPR, the lower is the time needed for the transformation. This is due to the larger number of collisions (and therefore the energy transferred to the powders) per unit time for high BPRs. As a result, the milling intensity is higher. The standard BPR used in laboratory mills is generally 10:1 [Jan 2005, Sur 2001].
- *Rotational speed*: The higher is the milling speed, the higher is the amount of energy transferred to the powder and, hence, the shorter will be the milling time. However, the final product can also be affected by the milling speed [Jan 2005, Sur 2001]. Furthermore, high milling speeds lead to a significant increase of the temperature of the vial.
- *Milling time*: This is one the most important parameters in ball milling [Sur 2001] along with the rotational speed. It is strongly correlated to the other milling