Review

Nanocrystalline Materials: Synthesis, Characterization, Properties, and Applications

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Abstract: Nanostructuring is a commonly employed method of obtaining superior mechanical properties in metals and alloys. Compared to conventional polycrystalline counterparts, nanostructuring can provide remarkable improvements in yield strength, toughness, fatigue life, corrosion resistance, and hardness, which is attributed to the nano grain size. In this review paper, the current state-of-the-art synthesis methods of nanocrystalline (NC) materials such as rapid solidification, chemical precipitation, chemical vapor deposition, and mechanical alloying, including high-energy ball milling (HEBM) and cryomilling was elucidated. More specifically, the effect of various process parameters on mechanical properties and microstructural features were explained for a broad range of engineering materials. This study also explains the mechanism of grain strengthening using the Hall-Petch relation and illustrates the effects of post-processing on the grain size and subsequently their properties. This review also reports the applications, challenges, and future scope for the NC materials.

Keywords: nanocrystalline materials; cryomilling; characterization; synthesis; mechanical properties; microstructures

1. Introduction

Material scientists and engineers have been working with conventional polycrystalline materials for decades. With the advancement in manufacturing and characterization techniques, researchers now have a much better understanding of materials and their properties. Due to the diverse applications and working conditions of materials, it is now a continuous and demanding requirement to improve upon the mechanical properties of these materials. Thus, it has attracted a lot of research interest in the past few decades. In polycrystalline materials, the principal mechanical properties are governed by the deformation mechanism, which occurs due to the movement of dislocations through crystallographic planes. This partial dislocation emission is more prominent at a finer grain size of 10–50 nm [1]. According to the Hall-Petch relationship, the mechanical strength of materials can be increased by reducing the average grain size [2]. On the basis of this relation and subsequent experiments conducted, scholars concluded that reducing the grain size to the nanometer range could provide better mechanical properties due to grain refinement strengthening [3]. There are several severe plastic deformation (SPD) methods to generate nanostructures on the surface of the material for applications that demand superior surface mechanical properties [4–7]. Studies on SPD techniques have shown promising results in producing nanostructured metal hydrides with enhanced hydrogen sorption properties [8]. However, these processes are generally costly due to extensive post-processing requirements, and that enhancement in the surface properties is limited to a depth of a few micrometers. To improve upon the bulk properties, the emphasis was on achieving the nanostructuring throughout the material. Thus, in 1984,
Birringer et al. [9] first introduced and popularized the concept of nanocrystalline (NC) materials. NC materials are single or multi-phase polycrystalline solids having an average grain size of less than 100 nm. Because of their incredibly small size, a significantly high-volume proportion of the grains are situated at the grain boundaries, which imparts unique properties to these materials [10]. Scholars revealed that NC materials possess remarkable mechanical properties when the grain size is in the nanometer range, hardness seven times higher, and yield strength ten times higher than conventional coarse-grain materials [11–13].

The grain size of the materials is classified into three categories: NC, ultra-fine grain (UFG), and coarse grain materials. Researchers summarized that NC material usually has a size less than 100 nm. When the grain size decreases from the micrometer range, NC materials showed a linear Hall-Petch (relation between yield strength/hardness and grain size). However, when the grain size is below 10 nm, NC material showed deviation from Hall-Petch. Dislocation pile-up is considered the primary mechanism for the reduced plastic flow when the grain size is in the micrometer range. The reduction in grain size accommodates more grain boundaries, which eventually act as a dislocation barrier in NC materials and provides enhanced mechanical properties. When the grain size is below 10 nm, a negative relationship also known as the inverse Hall-Petch relationship is observed [14].

Figure 1 illustrates the relationship between flow stress and grain size for NC, and UFG materials, which is demonstrated by the linear Hall-Petch relationship. With the reduction in grain size, the strength increases due to piling up of dislocation at grain boundaries, which resists the plastic flow and grain growth. With the reduction in grain size below 100 nm, i.e., in the NC regime, there is a slight deviation in the relationship, but it still holds true. Below 10 nm grain size the strength of materials starts to reduce, also known as an inverse Hall-Petch behavior.

![Figure 1. Schematic showing the variation of flow stress with grain size.](image)

There are several methods to produce NC material, and the choice of the process depends on the starting phase of the material. A few of the most influential and popular methods include rapid solidification [15], chemical vapor deposition [16], chemical precipitation [17], high energy ball milling (HEBM) [18], and cryomilling [12] process. Over the past two decades, there has been a sharp increase in the research conducted on NC materials and their manufacturing processes. Figure 2 shows the research publications on NC metals. It demonstrates the increasing interest of scholars in developing materials with nano-scale features to enhance their mechanical properties. Scholars have identified that nanostructuring could provide exceptional performance compared to conventional polycrystalline materials with coarse size. Since then, a lot of work has also been done to optimize the production process and obtain superior mechanical properties.
NC materials have nano-scale crystallite structure, which largely affects the deformation mechanism in these materials. This change in the deformation mechanism provides superior mechanical properties to NC materials [19]. Due to these nano-scale features, the NC materials have enhanced strength [20–22], improved fatigue life [23–25], superior wear resistance [26,27], improved hardness [20,28,29], higher specific heat [30,31], and improved coefficient of thermal expansion [32–34]. However, researchers also revealed that NC materials have lower ductility [35]. NC materials are prominently used in a wide range of applications such as for aerospace [36–38], structural [39,40], Micro-electromechanical systems (MEMS)/Sensors [41,42], chemical catalysts [43], magnetic materials [44] and nuclear applications [45].

This review article aims to provide a comprehensive overview of the synthesis and properties of NC materials. Section 2 of this article provides a brief overview of the recent advances in the most commonly utilized manufacturing techniques to produce NC materials. The focus of this article converges on the cryomilling process of nanostructuring and their effect on microstructural features that are explained in Section 3. Section 4 emphasizes the superior mechanical properties of NC materials. The applications, challenges, and future scope of NC materials are discussed in Section 5.

2. Processing of NC Materials

Over the past two decades, scholars have done a tremendous amount of work in understanding the benefits of nanostructuring in materials over conventional materials. In this process, the methods to generate and process these NC materials have also evolved over the years. Today there are a wide variety of processes that can be used to produce nanocrystals. The choice of method of production broadly depends on the starting phase of the material, such as solid, liquid, and gaseous. Figure 3 presents the different production methods for NC materials based on the starting phase of the material.

![Figure 3. Methods of NC material synthesis.](image-url)
Solid-phase NC materials synthesis is mainly used for metals and alloys. The commonly used method of bulk-nano structuring from the solid starting phase is mechanical alloying, cryomilling [46–50], HEBM [51–53]), and spark erosion [54–56]. In recent years bulk-nanostructurung using the cryomilling method got wide attention among scholars because of the energy-efficient nature compared to other NC production routes. Liquid phase NC materials synthesis includes processes, such as rapid solidification [57–60], electrodeposition [61–63], chemical precipitation [64,65], and sol-gel technique [66–68]. NC material synthesis in gaseous form is achieved by inert gas condensation [69–71], vapor deposition/sputtering [72–76], and plasma processing [77]. Recently, scholars have diverted their research interests towards several unconventional methods to produce nanocrystals using biological cells [78]. The material chosen for nanostructuring using a particular method depends on its chemical and physical properties. Apart from that, choosing an appropriate processing route plays a key role in determining the cost, time, yield (output), and subsequent applications of the final functional product. Scholars have been working on improving these processing techniques by adjusting the process parameters. They employ post-processing techniques to enhance the mechanical properties further. Some of the key synthesis processes, such as solid (e.g., Mechanical alloying), liquid (Rapid solidification and chemical precipitation), and gaseous (Vapor deposition) are presented below.

2.1. Rapid Solidification

Rapid solidification is a popular method of producing NC materials, and it is a substitute for conventional casting techniques. It can produce NC materials with significant properties such as hard and soft magnetic properties and finer grain size than cast materials [79]. Rapid solidification is a melting and quenching technique [80] for primary processing of aluminum-based alloys to achieve smaller grain size and have better solid solubility of the additives [81]. The first step of the rapid solidification process is to heat the solid metal well above its melting point until the metal phase changes to a molten liquid. After this, the metal is suddenly quenched which results in the formation of nano-scale crystals. This reduction in grain size offers enhanced mechanical properties, such as better strength, hardness, corrosion resistance, and high-temperature resistance [82–85]. Primarily there are three methods employed for the production process, namely (i) spinning, (ii) spraying, and (iii) surface melting [80]. Afonso et al. [86] utilized the spray forming process to produce NC aluminum alloys with 5 wt. % of nickel. In this process, the molten metal just 5% above its liquidus temperature was sprayed from a nozzle of diameter 6 mm along with a jet of nitrogen stream from the gas source. This sprayed powder was collected at the bottom in a collection chamber of the atomizer. Figure 4 shows a schematic diagram of the spray forming process for the rapid solidification technique to produce NC materials.

![Schematic diagram of spray forming process for rapid solidification to produce NC materials.](image)

**Figure 4.** Schematic diagram of spray forming process for rapid solidification to produce NC materials.

Recently, there has been a sharp increase in the number of research studies conducted on Fe-based alloys using rapid solidification. Ohodnicki et al. [60] utilized a rapid solidification technique followed by an annealing process to make amorphous Fe-based magnetic
alloys having NC phases. Their analysis confirmed the formation of body-centered cubic (BCC) and face-centered cubic (FCC) nano-scale crystallite structures embedded in the amorphous matrix. The microstructure showed distinctive areas rich in Fe, Ni, and B, respectively. These distinctions of element-rich phases are due to the BCC, FCC, and other inter-granular phases. Lee et al. [58] proposed that after rapid solidification of Fe-based alloys, the stability during thermal annealing post-process defines the physical properties such as uniform shape, size, distribution, and crystallization ratio of the crystallites formed, which in turn influences the soft magnetic properties of alloys. Ipatov et al. [59] studied the magnetic properties of Ni-based alloys (Ni-Si-B) for low-temperature structural applications synthesized by rapid solidification. They examined and compared the effect of the quenching and annealing process on the magnetic properties of the Ni-Si-B alloys. They varied the nickel content to prepare two variations of the alloy, one with 75% nickel content Ni75 (Ni75Si15B10) and the other with 80% nickel content Ni80 (Ni80Si10B10). Their results show that the Ni80 has a higher saturation magnetization at lower temperatures than Ni75. They concluded that the magnetic property increases with the increase in nickel content.

In summary, rapid solidification is an excellent process for producing NC material with improved properties. This process generally produces NC Fe and NC Ni-based alloys that offer better soft and hard magnetic properties. In summary, rapid solidification is an excellent process for producing NC material with improved properties. This process generally produces NC Fe and NC Ni-based alloys that offer better soft and hard magnetic properties.

2.2. Chemical Precipitation

Chemical precipitation is yet another method to obtain NC powders in bulk quantities. This method is mainly employed for chemicals and metal compounds that can precipitate out. This process involves a chemical reaction to create solid particle suspension in the solution. Due to this chemical reaction, the metals ions in the solution precipitate completely, resulting in a higher yield of NC powder. This method is primarily used to produce particles with NC grains with larger surface areas [87]. In this method, an ionic metal solution is treated with chemicals to precipitate the metallic ions. These precipitated metallic particles have an NC grain structure. Figure 5 shows the schematic process of the chemical precipitation method where di-ammonium hydrogen phosphate is added to calcium nitrate solution in a drop-wise manner. Simultaneously, Ammonium hydroxide solution is also added to maintain the pH of 11. This process is carried out with constant stirring leads to the formation of hydroxyapatite (HA) suspension. This suspension once settled at the bottom of the container can be extracted to give out HA particles with NC grain structure. Cellulose acetate/polyetherimide membranes with HA nanomaterials produced by this method are useful for adsorption and biomedical applications [88]. Priya et al. [64] synthesized NC perovskite with an average grain size of 300 nm using the chemical precipitation technique and studied its physical and chemical properties. Their XRD results revealed the presence of an FCC crystalline lattice structure. The authors performed the sintering of the NC perovskite pellets at 800 °C for 8 h and observed the reduction in average grain size to 100 nm.

Luna et al. [89] used the chemical precipitation method to synthesize spherical copper oxide particles with NC grain features. They performed annealing of the NC CuO at 200 °C, 300 °C, and 600 °C and reported the average crystallite size of around 15 nm, 16 nm, and 32 nm for each annealing process, respectively. Devi et al. [90] synthesized spherical cadmium sulfide nanoparticles by varying the temperature from 20 °C to 80 °C. They observed that the particle size and particle agglomeration increase at higher temperatures and the particles become more and more spherical. This CdS layer precipitation can be used as a window layer for solar cells applications. Ibrahim et al. [17] went ahead and doped the cadmium sulfide with manganese to prepare NC material using the precipitation technique. They were able to obtain fine grains in the size range of 7–8 nm. Lang et al. [91] used the doping technique to produce cerium doped zinc oxide particles with NC grains without
using any catalysts for the process. They were able to obtain grain sizes ranging from 8 nm to 20 nm for different concentrations of cerium. They proposed that this reduction in the size could be due to the formation of a compound of zinc with rare earth (RE) ions, i.e., RE-O-Zn, which constrains the growth of nanocrystals.

![Figure 5. Schematics of chemical precipitation method to synthesize HA powder with NC grains.](image)

Thus, in summary, the chemical precipitation can be used to produce NC materials in bulk quantities. This method is mainly employed for chemicals and metal compounds that can precipitate.

2.3. Chemical Vapor Deposition

In general, vapor deposition (VD) is a surface coating technique employed to enhance surface properties. This coated surface offers superior mechanical properties. In this process, the material is condensed onto a substrate to produce a solid layer through condensation, chemical reaction, or conversion. Since the deposited particles have grain sizes in the order of nano-scale, this method is effectively used to produce NC materials. In a typical chemical vapor deposition (CVD) process, a volatile substrate in the vapor phase is condensed onto a substrate to generate solid phase material [92]. Figure 6 shows the general schematic of the CVD process wherein a volatile material is exposed to the substrate material. This volatile material reacts or decomposes and condenses onto the substrate and form thin films. CVD process results in NC solid materials with excellent surface properties, and they are commonly used for applications in the semiconductor industries to deposit thin films with good surface characteristics.

![Figure 6. Schematic of the CVD process.](image)

Although the basic principle of the CVD process remains the same, a lot of research modification has been done over the past few years to cater to different kinds of NC materials. Recently, Kim et al. [93] used the catalytic chemical vapor deposition (CCVD) process to grow high-quality carbon nanotubes (CNT) on biomorphic carbon materials (BCMs) by the catalytic decomposition of hydrocarbon vapors. These carbon nanotube...
filters were developed for heavy metal adsorption. This method of production is very cost-efficient for the bulk synthesis of CNTs. Juggernauth et al. [94] used the CVD process and adopted step-wise control of various process variables such as gas flow, pressure, and time for the growth of films. This allowed them to successfully deposit the vanadium oxide structures into various functional shapes such as wires, ribbons, and platelets in the order of nano-scale. The process parameters to produce these CNT-mediated vanadium oxide structures could easily be altered for a variety of functional applications such as electrochemical cells, physical and chemical sensors, etc. Ariffin et al. [95] also reported a novel method. They used a cold-wall plasma-assisted CVD process to synthesize nitrogen-doped NC graphene layers on a polycrystalline Ni substrate at considerably lower temperatures of around 100 °C. This process could be used to develop transparent nano-scale devices soon. Ascencio-Hurtado et al. [96] used a plasma-enhanced chemical vapor deposition (PECVD) process to synthesize phosphorus-doped amorphous silicon-germanium (a-SiGe) thin-film embedded with high-efficiency nanocrystals at low frequency and temperature of 200 °C. The resultant thin films exhibit an excellent thermo-electric behavior. This material has prospective applications in the field of power generation.

To summarize, the CVD process is mainly employed to produce thin film coatings on the substrate material. This coated surface offers excellent mechanical and tribological properties [97,98].

2.4. Mechanical Alloying

Mechanical alloying (MA) is a solid-state powder processing technique involving the mechanical mixing of powders to produce composite metallic powders or alloys [99]. During milling, the metallic powders undergo repetitive cold welding and fractures, thus reducing the particle size [100,101]. This process was originally developed around 50 years ago to produce oxide-dispersion strengthened (ODS) Ni and Fe-based superalloys [102]. Figure 7 shows the process to create ODS superalloys using mechanical alloying and hot rolling heat treatment. In this process, the metal powders and dispersive oxide particles are mixed in a mechanical mill wherein it undergoes repetitive welding and fracturing to produce a composite powder. This powder is then post-processed using hot rolling to produce the final product. MA process is further classified into HEBM and cryomilling. HEBM is generally carried out at room temperatures, whereas the cryomilling process is carried out at cryogenic temperatures.

![Post-processing](image)

**Figure 7.** Flow chart showing the process to create ODS superalloys using mechanical alloying and hot rolling heat treatment.

2.4.1. High Energy Ball Milling

The HEBM process was introduced by John Benjamin at the International Nickel Company (INCO) in the late 1960s to produce Ni-based alloys [103]. They utilized the HEBM method to process metal powders. It was developed to cater combination of metals that could not be processed by other processing methods due to the considerable differences
in their melting point. In such cases, the materials had to be processed in their solid form using a cold deformation process. HEBM is one such process in which milling media (generally hard metallic balls) is used to mill the particles in a centrifugal cylinder. In this process, the material powder particles are plastically deformed and fractured repeatedly. Figure 8 shows the schematic of a typical ball milling process. Here, the direction of rotation of the milling bowl is opposite to that of the balls. Thus, friction resulted from the hardened milling balls and the powder mixture being ground alternately rolling on the bowl’s inner wall and striking the opposite wall. The impact energy of the milling balls in the normal direction attains a value of up to 40 times higher than that due to gravitational acceleration [104]. The crystallite size is reduced by repetitive cold-welding, fracturing, and re-welding of the particles. The result is a homogenous mixture of particles with NC grains structure. This process is mainly used to produce NC metal powders of aluminum, titanium, and their alloys [53]. The recovery and recrystallization due to heat generation because of friction is one of the downsides of this process and is difficult to control by any of its process parameters [105].

To summarize, the HEBM is the basic mechanical attrition process utilized to produce NC materials. The synthesis process involves mixing the metal powders and the milling media into a milling chamber. The rotation of this chamber caused the powder particles to undergo repetitive welding and fracturing thus, reducing the average particle size of the powder. This shearing and welding of particles, in turn, reduce the grain size of the milled material.

2.4.2. Cryomilling

Cryomilling is another prevalent method to produce NC materials that offer an improvement over the conventional ball milling process. Apart from providing mechanical attrition to cause repetitive fracturing and welding to reduce the particle size, the cryogenic temperatures of the chamber do not allow any recovery or recrystallization of grain size [105]. This leads to fine grain size and rapid grain refinement compared to other processes. In a typical cryomilling setup, the metallic powder or combination of powders is pre-mixed and put into an insulated attrition chamber. Along with the powder, milling balls typically made of tungsten carbide [52] or stainless steel (SS) [106] are added in a specific ball to powder ratio. Liquid nitrogen is continuously supplied into this cryogenic chamber to reduce the temperature to cryogenic levels. A control thermocouple is used to monitor the temperature of the attrition chamber continuously. The attrition is produced by an impeller dipped into the material slurry inside the chamber. The other end of the attrition shaft is generally connected to a driving motor, which drives the shaft. During the attrition process, the metallic powder particles undergo cold welding and then followed by fracturing and re-welding. This phenomenon repeatedly undergoes at cryogenic temperatures leading to the formation of nano-scale grains. Thus, the cryomilling process can be effectively used to produce bulk quantities of NC materials [107]. Figure 9 shows the setup for the cryomilling process at the University of Nevada, Reno. The setup shows the supply of liquid nitrogen from the storage tank to the attrition chamber through a flow control valve.
The process parameters for the cryomilling process, such as the milling rotations per minute (RPM), milling time, the radius of milling media, temperature, the ball to powder ratio, and addition of anti-agglomerates such as stearic acid, play an essential role in determining the properties of the obtained metal powders. Any variation in these parameters can lead to considerable variation in results. Mainly, the variations may occur in the crystallite size of the material or the presence of voids, which has a great impact on the mechanical properties of the final component. Several studies have been conducted to study the effect of the process parameters on the cryomilling process to obtain optimum process parameters. Table 1 shows the different processing routes and process parameters used by researchers to produce nanocrystalline materials.
**Table 1.** Processing route and process parameters for the mechanical alloying method.

| Materials | Additives | Processing Route | Process Parameters | Outcomes |
|-----------|-----------|------------------|--------------------|----------|
| AA5083    | Vanadium  | HEBM followed by | • Milling time = 100 h  
                      | (0.5 and       | spark plasma sintering (SPS) or  
                      | 5 wt. %)      | cold compaction (CC) |
|           |           |                  | • Milling RPM = 280  
                      |           |                  | • Intermittent milling (30 min cooling time after every hour) |
|           |           |                  | • Ball: powder = 16:1  
                      |           |                  | • 1.5 wt. % stearic acid (to avoid excessive cold welding) |
|           |           |                  | • Argon environment  |
|           |           |                  | • Post-processing:  
                      |           |                  | CC: 3 GPa pressure at room temperature.  
                      |           |                  | SPS: 600 MPa pressure at 400 °C |
|           |           |                  | • Higher Vanadium content resulted in finer grain size (≈100 nm).  
                      |           |                  | • Alloys processed by CC resulted in pores that increased with higher Vanadium wt. %. |
|           |           |                  | • SPS process eliminated the pores, thus increasing the density.  
                      |           |                  | • Best corrosion resistance for 5 wt. % Vanadium alloy. |
|           |           |                  | • Increased hardness for alloys having high solubility of Vanadium and <100 nm grain size. |
| Rhodostannite |           | Ball milling, SPS | • Feed = 100 g  
                      | Cu$_2$FeSn$_3$S$_8$ |                  | • 10 h |
|           |           |                  | • 30 kg of tungsten carbide balls, each 35 mm in diameter.  
                      | [52]          |                  | • Mill amplitude = 20 mm |
|           |           |                  | • Rotation speed = 960 min$^{-1}$  
                      |           |                  | • Argon atmosphere |
|           |           |                  | • SPS at 300–350 °C. |
|           |           |                  | • The stoichiometric ratio of elemental powders (Cu, Fe, Sn, and S) was taken for milling. |
|           |           |                  | • Crystallite Size ≈ 50 nm. |
|           |           |                  | • Low thermal conductivity was obtained. |
|           |           |                  | • Unreacted Fe mixed into the quaternary sulfide structures lead to the formation of stannite after SPS post-processing. |
| Al 5083   |           | Cryomilling, degassing, Hot  
                      | 440 C steel balls, each 6.35 mm in diameter.  
                      | [108]      | isostatic pressing (HIP), and  
                      | • Ball: powder = 10:1 Mass ratio.  
                      | Extrusion | • Milling time = 25 h  
                      |           |                      | • Vacuum degassing at 300 °C, 10$^{-6}$ torr.  
                      |           |                      | • HIP at 200 MPa, 523 K for 30 min in argon environment.  
                      |           |                      | • Extrusion at 523 K.  
                      |           |                      | • Extrusion Ratio = 9:1. |
|           |           |                  | • Obtained grain size = 25 nm to 35 nm. |
|           |           |                  | • Yield strength, ultimate tensile strength (UTS) increase by ~30% |
|           |           |                  | • No significant impact on percentage elongation. |
| AZ31      |           | Cryomilling,      | • Liquid nitrogen at −196 °C for cryogenic cooling.  
                      | powders  |
|           |           |                  | • AZ31 Powder = 6 g in 50 mL grinding vessel.  
                      | [109]     |                  | • SS balls 25 mm in diameter. |
|           |           |                  | • Argon gas atmosphere.  
                      |           |                  | • Precooling at 5 Hz for 18 min |
|           |           |                  | • Grinding at 22 Hz for 5 min  
                      |           |                  | • Intermediate cooling at 5 Hz for 3 min.  
                      |           |                  | • Cryomilling time = 15 min to 8 h. |
|           |           |                  | • The average crystallite size is 26 nm after 6 h of milling. |
|           |           |                  | • Hardness = 162 HV after 6 h of milling. |
Table 1. Cont.

| Materials | Additives | Processing Route | Process Parameters | Outcomes |
|-----------|-----------|------------------|--------------------|----------|
| 2024 Al alloy [106] | Spray atomization, Cryomilling, Sintering | • Milling RPM = 300  
• Milling Time = 20 h  
• Milling temp. = −193 °C  
• Ball: Powder = 4:1  
• Diameter of SS ball = 6.4 mm  
• Liquid nitrogen is used as a coolant and lubricant for milling.  
• Powder kept in argon environment glove box to remove nitrogen.  
• High vacuum sintering for 5–20 min at 475–525 °C. | • Crystallite size reduces with the reduction in particle size due to fragmentation of particles and a rise in the number of defects in the lattice structure.  
• Obtained crystallite size is less than 25 nm.  
• Achieved powders are not rounded and have flaky textures. |
| 5083 Al Alloy [110] | Gas Atomization, Cryomilling, CC, SPS | • Milling RPM = 180  
• Milling time = 8 h  
• Cryogenic fluid = Liquid nitrogen  
• Ball: Powder = 32:1  
• Diameter of SS balls = 6 mm  
• CC Load = 908 Kg for 1 min.  
• Sintering temperature increased from RT to 350 °C in 180 s.  
• Sintering temp. (hold) = At 350 °C for 120 s.  
• Sintering pressure = 80 MPa. | • Avg. grain size after cryomilling = 25 nm  
• Avg. particle size after cryomilling = 10–50 µm.  
• Grain size after sintering = 50 nm.  
• The outer surface of particles had a coarser grain structure. |
| Al [107] | Cryomilling | • Single tungsten carbide ball  
• Cryogenic fluid = Liquid nitrogen (less than −150 °C)  
• Milling vibrational amplitude = 1.5 mm  
• Argon supply rate = 1 l/h  
• Ball: Powder = 80:1  
• Milling time = 6 h 30 min. | • Average grain size after cryomilling = 7–10 nm.  
• Grains are stable up to 100 °C temperature. |
Table 1. Cont.

| Materials | Additives | Processing Route             | Process Parameters                                                                 | Outcomes                                                                                                                                 |
|-----------|-----------|------------------------------|-----------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------|
| AA5083    | 0.15 wt. % graphite | Acoustic mixing, Cryomilling, Degassing, laser welding | • Mixing acceleration = 10 g (g-force) for 1 h.<br>• Ball: Powder = 32:1<br>• Diameter of SS balls = 0.25 in.<br>• Milling time = 2, 4, or 8 h.<br>• Powder kept in Argon environment glove box to remove nitrogen.<br>• Powder yield 830–870 g.<br>• Degassing in flowing argon environment at 350 °C for 6 h and allowed to cool in the furnace.<br>• Laser welding power is 50 W at 5, 10, 50, 100, and 150 mm/s traverse speeds. | • Hot cracking issue occurs during laser melting due to the formation of spinel phase<br>• During cryomilling, the nitrogen gets dissolved within the Al matrix-forming Aluminium nitride that acts as grain pinner sites for finer grain growth.<br>• 8-h cryomilled alloys showed superior laser welding property due to reduced oxide layer.<br>• Crystallite size for 8 h cryomilled powder is 22 nm.<br>• Crystallite size for cryomilled and degassed powders is 29 nm.                                                                 |
| Si        |           | Cryomilling, Etching, Functionalization | • Milling temp. = −73.15 °C (Nitrogen)<br>• Milling time = 10 h<br>• Argon environment for milling.<br>• Etching of 5 mg of particles in 1 mL of ethanol by HF: HNO₃ in the ratio 10:1. Etching time = 10, 30, 60, 120, and 300 s.<br>• Sonification was performed after cryomilling and etching for 10 min each.<br>• Particle functionalization by stirring at 120 °C for 10 h. | • Obtained dual-phase nanocomposite with the mean grain size of 80 nm.                                                                                                                                 |
| Al        | 5 wt. % Mg | Cryomilling followed by SPS     | • Milling time = 2, 4, 6, and 8 h.<br>• Ball to powder ratio = 30:1<br>• Added stearic acid to prevent agglomeration.<br>• Liquid nitrogen.<br>• Diameter of SS balls = 6 mm.<br>• Milling time = 8 h<br>• Cryogenic fluid = Liquid nitrogen. | • After 8 h of cryomilling the average crystallite size reduced from 70 nm to 28 nm for pure Al powder and to 20 nm for Al 5 wt. % Mg.<br>• For Al-5 wt. % Mg crystallite size reduced to 20 nm after 8 h of cryomilling.<br>• Increased hardness 290 HV for 8 h cryomilled and SPS samples.<br>• UTS is determined as 466 MPa for 6 h of cryomilling for SPS samples.                                                                 |
For the cryomilling process, milling at cryogenic temperatures caused embrittlement of the particles, which allows repetitive fracturing and cold-welding of soft materials and highly plastic materials [105]. In general, the particle size reduces with the increase in cryomilling duration due to repeated fracturing and welding, reducing the grain size to the nanoscale. However, after a certain duration of time (around 6 h), there is no considerable change in the grain size due to the agglomeration of the particles [109]. Beyond this, continued milling will not result in any considerable change in crystallite size. Another most critical factor in the cryomilling process is the milling time. Guan et al. [109] performed cryomilling of AZ31 alloy powders with 25 mm SS milling media for 15 min to 8 h. The cryomilling consists of precooling, grinding followed by cooling cycles. The authors concluded that the ideal time for cryomilling should be 6 h because there was no significant change in the crystallite size (26 nm after 6 h of milling) of the alloy particles. Despite these conclusions, the research group typically tends to do the cryomilling for 8 h to maximize the reduction in crystal size, avoiding the scope of error. Kumar et al. [107] worked with aluminum particles in bulk quantities. They performed cryomilling with a single tungsten carbide (WC) ball for 6 h 30 min and obtained crystallite size as low as 7–10 nm. These grains were stable at high temperatures up to 100 °C.

To determine the bulk properties of these NC materials and make them functional, they need to be post-processed using suitable techniques such as hot isostatic pressing (HIP), SPS, etc. Tellkamp et al. [108] worked on the cryomilling of spray atomized 5083 Al powder for 25 h, followed by degassing at 300 °C to obtain a grain size of 25–35 nm. The processing was performed by the HIP method at 200 MPa, 523 K for 30 min in an argon environment followed by extrusion. The authors observed that the material bulk properties such as yield strength and UTS in the extruded material showed an improvement of approximately 30%. However, no significant change in percent elongation was detected. Dementrio et al. [106] studied the effect of the crystallite size on the phase transformation of cryomilled Al 2024 alloy during the sintering process. They observed that for the smaller particles, the phase transitioning from the Al$_2$CuMg (S) to the Al$_2$Cu ($\theta$) phase was occurred faster due to the higher amassed deformation energy. Ye et al. [110] performed cryomilling with gas atomized 5083 Al alloy, with the ball to powder ratio of 32:1. The cryomilled powders were post-processed by CC at a load of 980 Kg for a min and followed by sintering at 350 °C at 80 MPa pressure for 120 s. They observed the change in average grain size from 25 nm after cryomilling to 50 nm post sintering process. Menezes et al. [111] conducted cryomilling of Al and Al-5 wt. % Mg for 2, 4, 6, 8 h followed by SPS to make the bulk samples. They found that the average crystallite size for pure Al decreased from 70 nm to 28 nm after 8 h of cryomilling. For Al-5 wt. % Mg powder the crystallite size was reduced to 20 nm after 8 h of cryomilling. They also studied the mechanical properties of cryomilled SPS samples and concluded that a decrease in crystallite size increases the hardness to 290 HV for 8 h cryomilling and ultimate tensile strength to 466 MPa for 6 h cryomilling.

In summary, the cryomilling process is one of the most popular methods to synthesis bulk NC materials. It combines the benefits of both mechanical attrition and cryogenic temperatures. The mechanical attrition treatment reduces the grain size, and the cryogenic environments prevent recovery and recrystallization. However, several studies have been conducted to estimate the appropriate duration for cryomilling for different metals and alloys, which recommends the ideal time of around 6 h, beyond which there is little change in the grain size. Thus, further milling the powders will not offer any significant benefits, resulting in energy wastage.

### 3. Microstructural Features of NC Materials

Over the past two decades, scholars have adopted mechanical alloying (MA) methods, such as HEBM, cryomilling, and other techniques like rapid solidification, chemical precipitation, and CVD to produce NC materials. These techniques have resulted in NC materials with superior mechanical properties. Researchers have correlated them with
microstructural features, such as grain size, phases, crystallite size, and lattice parameters, to understand the nature of these properties. Guan et al. [109] studied the effect of cryomilling time on the microstructural evolution of AZ31 powders containing particle sizes ranging from 38 µm to 75 µm. In addition to that, they demonstrated the effect of cryomilling time on particle morphology and grain size. The cryomilling experiments were performed in liquid nitrogen media from 15 min to 8 h at −196 °C. The authors observed that cryomilling for 1 h led to particle agglomeration and subsequent increase in the size of the particle. The authors revealed that coarse particles started breaking down with an increase in cryomilling time, and the observed particle size after 6 h of cryomilling was 26 µm. Therefore, the authors recommend that 6 h of cryomilling is optimum for AZ31 powders because the insignificant grain size reduction is beyond 6 h. The authors attributed cold welding and repetitive fracture as the primary mechanism for developing particle morphology during cryomilling, and other scholars also reported similar findings [5,112] In the initial phase of cryomilling, cold welding dominates over the fracture, leading to increased particle size. As the deformation continues for a more extended period, fracture dominates over cold welding, which causes a reduction in particle size. Figure 10 represents the transmission electron micrographs (TEM) of AZ31 powders cryomilled for 3 h, 6 h, and 8 h and the corresponding grain size distribution. The reported grain size for 3 h, 6 h, and 8 h cryomilled AZ31 powders are 42.4 ± 12.2 nm, 26.2 ± 7.9 nm, and 26.1 ± 7.2 nm.

Youssef et al. [50] manufactured bulk NC Al-5 wt. % Mg by mechanical alloying and studied its mechanical properties. They revealed that the NC alloy showed four-fold high
strength with enhanced ductility of 8.5% compared to conventional Al-5083. Furthermore, the XRD analysis of bulk NC materials revealed the formation of Al-Mg solid solution, which is also correlated to the increase in lattice parameter. They also revealed that bulk NC material showed a broadened peak with reduced peak intensity, attributed to grain refinement and lattice strain during milling. Guan et al. [113] performed cryomilling on AZ31 powder particles with sizes ranging from 38 µm to 75 µm followed by SPS at 350 °C, 400 °C, and 450 °C and revealed that these processing routes provided remarkable mechanical properties for AZ31 alloy. The cryomilling experiments were performed in liquid nitrogen media at −196 °C for 6 h with a shaking frequency of 22 Hz. Furthermore, the authors divulged that those optimum mechanical properties were observed for samples sintered at 400 °C because of full densification and minimum grain growth during sintering. The enhanced mechanical properties are due to synergistic strengthening from grain refinement, solid solution, and dispersion due to oxides. Scanning electron micrographs (SEM) of as-received AZ31 powder particles showing particle size and morphology which is represented in Figure 11a. The average size of the as-received powder particles revealed from SEM is 2.03 ± 0.47 mm, which is shown in Figure 11b. The particle size morphology after cryomilling for 6 h is shown in Figure 11c. After cryomilling for 6 h, the observed grain size from XRD analysis is 32 nm and from TEM analysis is 26.2 ± 7.9 nm. This is a clear indication that cryomilling effectively reduces the grain size. This reduction in particle size is due to fracturing, cold welding and re-fracturing of the particles during the milling process. Figure 11d shows the fracture sites (indicated by yellow arrow) where the particle has sheared under the forces of milling media. The figure also shows the cold-welded sites (indicated by white arrow) where the sheared pieces broken off from different particles have cold-welded together at cryogenic temperature to form one big particle. This repetitive process of shearing and cold-welding continues for entire duration of the cryomilling.

Figure 11. SEM images of (a) as-received powder; (b) internal grains; (c) 6 h cryomilled powders; (d) cold welding (indicated by white arrow) and fracture process (indicated by yellow arrow). Reproduced with permission [113]. Copyright Elsevier, 2016.

The cold welding and fracture during cryomilling are responsible for the evolution of particle morphology. During the cryomilling process, the milling media plastically deforms the powder particles and leads to work hardening and fracture. The newly formed fracture surfaces promote cold welding and increase the particle size. As the deformation continues, the fracture becomes dominant over cold welding and reduces particle size. When the milling times increase beyond a specific limit, cold welding and fracture reach an equilibrium state, and particle size won’t change with additional milling time. Scholars indicated that the optimum cryomilling time for better mechanical properties

[0x0]15 of 31

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of bulk NC materials is 6 h \cite{3,114}. Park et al. \cite{114} fabricated NC bulk Al-7.5 wt. % Mg using cryomilling technique followed by extrusion, and they performed microstructural investigation based on various extrusion temperatures. The extrusion temperature chosen for their experiment is approximately $\pm 25 \times 0.5 \, T_m$ (melting temperature). The authors revealed that alloy extruded at low extrusion temperature is less anisotropic, and they showed a tendency to rotate in a direction parallel to the extrusion direction and have a smaller grain size. In their experiments, Khan et al. \cite{18} synthesized Mg-Al alloy containing 0 wt. % to 20 wt. % of Al by means of HEBM followed by compaction under a pressure of 3 GPa at room temperature (RT). In addition to that, the authors heat-treated the Mg alloys from RT to 425 °C for 1 h. The grain size of the HEBM’ed Mg powder was $67 \, \pm \, 17.7 \, nm$ and grain size decreased with increased wt. % of Al. The authors observed new peaks, peak broadening, and peak shifts with the addition of different wt. % of Al to the Mg. In addition, when 5 wt. % Al added to Mg no new peaks showed in the XRD plot represented in Figure 12.

![Figure 12. XRD plots (a) unmilled Mg and 100 h milled Mg containing different wt. % of Al, indicating peak broadening, peak shifts and evolution of secondary phase (b) zoomed region showing peak shifts. Reproduced with permission \cite{18}. Copyright Elsevier, 2004.](image)

This reveals that the Al is fully dissolved in Mg, and no new phases were formed. XRD analysis of 10 wt. % Al and 20 wt. % Al in Mg showed the formation of new phases and formation of secondary phase Mg$_{17}$Al$_{12}$. The increased wt. % of Al addition to the Mg caused the peaks to shift to a higher Bragg angle, which is attributed to the increase in lattice parameter. The XRD experiments performed at high-temperature (HT) revealed that for Mg and Mg-5 wt. % Al peak shifted towards low Bragg angle. However, Mg-10 wt. % Al and Mg-20 wt. % Al shifted towards higher Bragg angles. The authors observed significant grain growth for Mg-10 wt. % Al and Mg-20 wt. % Al compared to Mg and Mg-5 wt. % Al at HT. This is because of the higher grain refinement of Mg-10 wt. % Al and Mg-20 wt. % Al, which causes a high amount of stored energy, acts as a driving force for grain growth at HT. Figure 13 represents the grain size variation with different heat treatment temperatures Mg and Mg containing different wt. % of Al. It is evident from the figure that for Mg-10 wt. % Al and Mg-20 wt. % Al showed a higher grain growth rate at a temperature higher than 300 °C.

Similar findings were reported by Esquivel et al. \cite{115} for Al-5 at. % Ni and Al-5 at. % vanadium alloys synthesized using HEBM. They summarized that alloying element and heat treatment temperature strongly influenced the thermal stability and hardness of the bulk NC materials. Sasaki et al. \cite{116} studied mechanical properties and microstructural features of NC Al-5wt. % Fe synthesized by MA followed by SPS. The authors adopted three different MA times: 60 h, 100 h, and 150 h. The SEM images of the MA’ed powders are represented in Figure 14. Fe particles are with bright contrast are uniformly dispersed in the Al powder. It is evident from the figure that both powders were homogenously mixed after 60 h of MA. As MA time increases, the volume fraction of Fe is reduced in Al powders due to the supersaturated dissolution. These alloys also exhibited high compression strength of
more than 1000 MPa at RT and 500 MPa at 350 °C, which attributed to the NC size of the grains.

![Grain size variation with temperature for Mg and Mg containing different wt. % of Al.](image)

**Figure 13.** Grain size variation with temperature for Mg and Mg containing different wt. % of Al. Reproduced with permission [18]. Copyright Elsevier, 2004.

![SEM images of MA of powders for (a) 60; (b) 100, and (c) 150 h.](image)

**Figure 14.** SEM images of MA of powders for (a) 60; (b) 100, and (c) 150 h. Reproduced with permission [116]. Copyright Elsevier, 2009.

In summary, NC materials showed superior mechanical properties attributed to the formation of NC grains developed due to different synthesis methods. These materials can provide high strength and hardness compared to conventional polycrystalline materials. Cryomilling has been considered the most popular synthesis method for NC materials. The optimum cryomilling time for better mechanical properties of bulk NC materials is 6 h. However, cryomilling for more than 6 h leads to minor enhancement of mechanical properties and is a waste of resources from an economic point of view.

4. Mechanical Properties of NC Materials

Over the past two decades, a lot of research has been conducted on the nanostructuring of commonly used metal and alloys for functional applications. The reduction in the grain size leads to the accumulation of grain boundaries over a smaller region, which acts as a hindrance to dislocation movement and cracks propagation, thus providing superior mechanical properties [117]. Studies have shown that these NC materials have far enhanced mechanical properties, such as increased strength, high specific heat, increased hardness, low thermal conductivity, increased fatigue life, and magnetic properties over the conventional polycrystalline materials [33,118,119]. Table 2 presents the generic effect of nanostructuring on the principal mechanical properties of materials based on the available research works conducted in the past. In this section of the article, the effect of reduction in grain size on the mechanical properties of NC materials will be reviewed.
Table 2. Effect of nanostructuring on principle mechanical properties.

| Mechanical Properties          | Increase/Decrease | Reference |
|-------------------------------|-------------------|----------|
| Yield strength                | Increases         | [20–22]  |
| Fracture strength             | Increases         | [20,21]  |
| Ductility                     | Decreases         | [35]     |
| Specific heat                 | Increases         | [30,31,120] |
| Hardness                      | Increases         | [20,28,29,121] |
| Magnetic property             | Increases         | [58–60]  |
| Thermal conductivity          | Decreases         | [122]    |
| Fatigue life                  | Increases         | [23–25,119] |
| Corrosion resistance          | Increases         | [53,123] |
| Electrical resistivity        | Increases         | [124]    |

For structural applications, material strength is the first and one of the most important mechanical properties to be considered. Studies have shown that the reduction in grain size results in higher yield strength for NC metals and alloys than their unprocessed raw counterparts due to grain refinement strengthening. The relationship between the yield stress and the reduction in grain size is given by the Hall-Petch equation as shown below [33]. Here, $\sigma_y$ is the yield stress (MPa), $\sigma_0$ is the friction stress (MPa), $d$ is the average grain size and $k$ is the constant.

\[
\sigma_y = \sigma_0 + kd^{-1/2}
\]  

This relation is crucial in understanding the effects of NC grain sizes on the mechanical properties of materials. Liu et al. [20] performed the mechanical milling of titanium powders and studied the relationship between the milling time, crystallite size, and the yield strength of the material. The authors observed that a reduction in crystallite size with the increase in milling time. This reduction in crystallite size increased the yield strength of material up to four times as compared to the unmilled titanium powders. In a similar study for titanium alloys, Deng et al. [21] prepared Ti-45Al-8Nb alloys with UFG structure using the cryomilling process followed by SPS at 900 °C, 1000 °C, and 1100 °C. They studied the compression properties of the prepared samples and at room temperature and observed that the alloys showed yield strength of up to 1575 MPa and fracture strength of 2627 MPa with strain at 23.5%. In addition to that, they conducted high-temperature compression tests at 850 °C and witnessed yield strength and fracture strength values of 955 MPa and 1041 MPa, respectively. Figure 15 shows the compression stress-strain curve for tests conducted for the cryomilling process followed by SPS at different sintering temperatures. The results indicate that the compression stresses and strains are much higher for higher sintering temperatures due to grain refinement strengthening. Although crystallite size is an important factor in determining the strength, the corresponding arrangement of adjacent grains also plays a vital role. Recent studies on NC aluminum alloys have shown materials with low angle grain boundaries have twice as much yield strength than high angle grain boundary materials because of the higher energy required to initiate the grain boundary sliding [125]. Thus, it can be concluded that reduction in grain size leads to grain strengthening, which gives NC metals and alloys their excellent strength properties.

Ductility is yet another mechanical property studied in combination with strength determination. In general, for a coarse grain material, the ductility increases with the reduction in the grain size. However, this trend changes when the grain size is reduced further. Studies on NC materials with grain size less than 25 nm showed that the reduction in grain size below 25 nm leads to decreased/limited Young’s modulus of NC metals and alloys compared to their coarser grain counterparts, as shown in Figure 16 [126]. This can be attributed to the inherent pores created during processing, unstable grain clustering under tensile stress, and crack nucleation [33]. Youssef et al. [50] fabricated NC Al-Mg alloy with high strength, 4 times as high as 5083 Al alloy. However, the achieved ductility value was limited to 8.5%, which is lower than the conventional 5083 Al alloy at around 12%. A lot of research has been conducted recently to achieve the optimal
combination of strength and ductility in the NC materials. Osman et al. [22] experimented with cryomilled and quasi-isostatically forged pure titanium metal and studied their tensile mechanical properties. They obtained high yield strength and UTS of 840 MPa and 902 MPa, respectively, with a high ductility of around 27.5%. They concluded that the reasons for the increased ductility were the presence of coarse grains (larger than 1000 nm), which suppressed the crack growth, propagation, the high angle grain boundaries in the structure, and degassing process, which removed all the elements that cause embrittlement. Thus, specific modifications to the structure can help in overcoming the obstacle of limited ductility in NC materials.

The reduction in grain size also impacts the fatigue and creep behavior of the functional components. Fatigue life determines the number of loading cycles a component can undergo before failing under the fatigue load. This type of failure generally occurs at much lower load values than the UTS. Since NC materials are being used in a variety of structural and functional applications, it is very crucial to study their fatigue behavior. However, very few studies have been conducted on their fatigue and creep behavior. Hanlon et al. [119] studied the fatigue behavior of cryomilled aluminum alloys and revealed that the reduction in grain size had increased the fatigue life. However, the crack initiation and propagation at a lower load ratio was much higher for a smaller grain size. Figure 17 shows the stress versus cycles to failure plot for NC, UFG, and micro grains. It can be easily interpreted from the plot that the fatigue life increases with the reduction in grain size. They also obtained similar results for pure titanium. Studies were also conducted on the creep behavior of NC materials to determine the stability of NC materials. Creep is a slow process wherein the material permanently deforms under continuous mechanical stresses over an extended period. Creep occurs at a much lower load than yield strength. Gollapudi et al. [127] studied the creep behavior of ball-milled NC aluminum as a function of grain coarsening resulting from the continuous mechanical stresses. Their studies revealed the role of grain boundaries in the deformation process. Kottada et al. [128] the creep behavior of NC Nickel at low temperatures and found similar results. Even at cryogenic temperatures, the creep behavior was evident due to grain growth [129]. Still, a lot more studies need to be conducted to develop an overall understanding of the fatigue and creep behavior of NC materials.

![Figure 15. Compression stress-strain curve for different sintering temperatures conducted at Room Temperature. Reproduced with permission from [21]. Copyright Elsevier, 2019.](image-url)
Apart from the yield stress, other mechanical properties such as hardness also behave in accordance with the Hall-Petch relationship. Chen et al. [130] determined the hardness of NC copper with an average grain size of 10 nm and confirmed that the hardness increases with the decrease in the grain size. They also measured the strain rate sensitivity of NC copper at 0.06 ± 0.01 and stress activation volume of 8b³ that indicated a surge in grain boundary activities. Yet, these properties did not dominate the plastic deformation in NC Cu. Liu et al. [20] also measured the average strain rate sensitivity for pure titanium milled for different durations and found that the average strain rate sensitivity decreases with a decrease in the grain size or increase in milling time. Recent computational studies on NC materials indicate an improved coefficient of thermal expansion [32]. Dong et al. [122] proposed a theoretical model to study the influence of grain boundaries and grain size on the thermal conductivity of NC materials. Their studies revealed that grain boundary effect and size effect reduces with an increase in grain size. However, the grain size effect on the thermal conductivity increases. Zeng et al. [124] studied the electrical properties of NC Gd metal and observed that the electrical resistivity increases with the decrease in the grain size.

![Figure 16](image-url)  
**Figure 16.** The variation of Young’s modulus with the grain size for Ni-P. Reproduced with permission from [126]. Copyright Elsevier, 2006.

In addition to bulk mechanical properties, nano crystallization could also improve the surface properties of materials. Studies have shown that NC materials have superior wear resistance due to increased hardness and better corrosion resistance due to the formation of a thin protective layer [131]. Yousefi et al. [132] prepared NC Fe-Ni permalloy and Fe-Ni-TiO₂ composite coatings using the pulse electrodeposition method and studied their surface properties. They measured the wear using pin-on-disk tests with an applied vertical load of 3 N, rotating at speed of 5 cm/s for a sliding distance of 250 m. The movement radius of the pin was 5 mm. Figure 18 shows the variation of coefficient of friction (CoF) and wear rate...
for coatings prepared at different applied current densities. It is evident from the plots that the Fe-Ni-TiO\textsubscript{2} coatings exhibit lower CoF and reduction in wear rate as compared to Fe-Ni permalloy. They stated that these improvements in properties are due to grain refinement and dispersion strengthening of the Fe-Ni-TiO\textsubscript{2} sample. Similarly, Liu et al. [133] studied the surface properties of NC Ni-Mo coatings synthesized by ultrasound-assisted pulse electrodeposition method. Their results revealed improvement in microhardness of Ni-Mo coatings with the reduction in crystallite size and increasing Mo content. This increase in microhardness helps to reduce the plastic deformation, which results in superior wear resistance of Ni-Mo coatings. Alternatively, Druga et al. [134] discovered that for Ni–W alloy coating, both wear rate and CoF are significantly increased by the presence of a prevailing amorphous phase. Hussein et al. [135] studied the mechanical and tribological properties of NC TiN deposited using the CVD process. The crystallite size of deposition is 10.33 nm and deposition layer thickness is 5 \textmu m. Their results showed a high hardness of 38.63 GPa, a higher modulus of elasticity of 358 GPa, and lower CoF. The NC coating also showed higher resistance to plastic deformation as compared with the uncoated sample, thus reducing the wear rate. Almangour et al. [136] used the HEBM process to produce H13 steel with 15 Vol. % of TiC nanocomposite powder which was post-processed using selective laser melting (SLM) process to obtain uniformly dispersed nanoscale TiC particles with a mean size of 50 nm. The resultant composite showed high hardness and elastic modulus with a reduced CoF of 0.526 and a reduced wear rate of 26%. They proposed that these improvements are an effect of grain boundary strengthening and grain refinement.

![Figure 18](image.png)

**Figure 18.** Plots showing the variation of (a) CoF and, (b) wear rate with different applied current densities at which the coatings were prepared. Reproduced with permission from [132]. Copyright Elsevier, 2018.

Materials are often exposed to environmental factors, such as moisture, heat, acidity, or alkalinity, which influence the service life of materials. Corrosion is one such phenomenon, which needs consideration when studying the properties of materials for application purposes. To overcome this issue, Sotniczuk et al. [137] conducted experiments with NC Ti and observed that annealing at lower temperatures can improve the corrosion properties by forming a passive layer on the surface. Javadhesari et al. [138] prepared NC Ti-50 at. % Cu alloy with 23 nm average grain size for biomedical applications. They reported that the Ti-Cu alloy shows a higher corrosion rate than Ti because of the thin layer of TiO\textsubscript{2} due to surface oxidation in the Ti sample. This oxide layer which prevents the corrosion in the Ti sample is absent in the Ti-Cu alloy sample. Zhuo et al. [139] optimized the flexible friction behavior using a movable friction instrument with flexible biological bristles to improve upon the coating properties of NC nickel. Their results revealed that under a controlled contact pressure between the friction medium and coating, the average crystallite size reduces by 3.3 nm resulting in a more compact, smooth, and improved
corrosion-resistant surface. They also reported that with this reduction in particle size, the hardness of the coating also increases by 12.6%. Firouzi-Nerbin et al. [140] prepared a coating of NC Ni-Cr alloy using the pulse electrodeposition method to study the corrosion properties of the coating. Based on the potentiodynamic polarization test, they reported that Ni-11.2 wt. % Cr alloy coating exhibits the highest corrosion resistance, which is attributed to the formation of a passive film. The corrosion resistance increases with the increase in the Cr content, however, shows a decreasing trend beyond 24 wt. % Cr, which is due to micro-cracks development. Their studies also show a decrease in the crystallite size from 114 nm to 66 nm when the Cr content increases up to 24 wt. % in the alloy.

Cheng et al. [141] conducted similar studies with NC Ni-saccharin coating and found that the corrosion resistance increases with the decrease in crystallite size. The decrease in crystallite size from 32.40 nm to 13.05 nm was achieved by the addition of saccharin. Li-yuan et al. [142] used saccharin to reduce the crystallite size of Ni in the range of 16 nm to 258 nm. They showed that the reduction in crystallite size increases the grain boundary density which in turn improves the corrosion resistance by accelerating the formation of passive layer for NaOH and NaCL solutions. In an acidic setup with H2SO4 solution, the corrosion resistance decreases with a decrease in crystallite size due to no passive layer formation. Esteves et al. [123] utilized the HEBM process to mill AA5083 alloys to the average grain size of 100 nm. Further, they studied its corrosion properties using cyclic potentiodynamic polarization (CPP) by comparing it with gas atomized powder and AA5083-H116 commercial alloy. Figure 19 shows the comparison of CPP curves for as received and HEBM’ed 5083 Al alloy consolidated by CC and SPS with the commercial alloy AA5083-H116. The current density of CC’ed HEBM 5083 Al alloys samples was higher than the as-received CC specimen due to the presence of large pores. The authors observed that the cryomilled samples with NC grains were less prone to corrosion due to significant grain refinement and homogenous structure.

Figure 20 shows the SEM micrographs for SPS’ed as received and HEBM’ed 5083 alloys. It is evident from the images that HEBM’ed samples underwent lesser corrosion on their surface. Thus, they were able to obtain AA5083 alloys that were high strength, hardness,
and greater corrosion resistance. Gupta et al. [143] also used the HEBM followed by SPS to obtain aluminum and Al-20 wt. % Cr alloys with high strength and corrosion resistance. Their studies revealed that the nanostructuring provided better corrosion resistance significantly for both aluminum and Al-20 wt. % Cr alloys. They reported that the lower anodic current density of SPS alloys provided a substantial passive region, which helped in reducing the rate of corrosion.

![Figure 20](image-url) SEM for (a) SPS as-received (b) SPS HEBM 5083 alloy after 24 h in 0.6 M NaCl solution. Reproduced with permission from [123], Copyright Elsevier, 2021.

Overall, the development of NC materials has improved mechanical properties over conventional coarse grain materials by fine-grain strengthening from grain refinement. In addition, NC materials show excellent strength properties with limited ductility. These properties can be well utilized to cater to a variety of applications. Scholars are now shifting the focus to enhance other mechanical properties of NC materials to broaden the spectrum of their applications.

5. Applications, Challenges, and Future Scope

NC materials are an advanced class of materials that have enhanced mechanical properties and are easy to produce and post-process in bulk quantities. Owing to these features, NC materials can be effectively used in a wide variety of applications, including aerospace, structural, nuclear, chemical, and automotive industries. Figure 21 shows a few applications of NC materials. Sevillano et al. [39] studied the tensile properties of NC materials and obtained high yield strength and fracture strength for the NC materials hence justifying its use in structural applications. Use of high strength, lightweight materials such as NC Aluminium can be used to produce aircraft and automobiles, which can increase their load-bearing capacity in turn saving a lot in terms of fuel consumption [144]. Other than automotive, NC materials are also useful in military and defense applications such as use in ballistic materials and armored military vehicles [145].

Nanostructuring is very helpful in improving magnetic properties in magnetic materials. A lot of studies have also been conducted to study the magnetic properties of NC materials with base metal as Fe or Ni for magnetic applications [44,58–60]. Researchers have also worked on synthesizing NC ferroelectric ceramics, which would harvest power from the mechanical vibrations of aerospace vehicles [38]. NC materials are widely used in sensors and semiconductor applications as well. Hegazy et al. [37] worked on the characterization of nanocrystals of cadmium selenide (CdSe) to be used in semiconductors for aerospace applications. They also studied the optical properties of nanoparticles and proposed their applications for solar cell technology and chemical sensing. Another application for solar technology is the use of thin films for windows produced by the chemical precipitation of CdS, which can act as solar cells. Baghbanan et al. [41] utilized the electrodeposition process to produce NC Nickel for MEMS to be used in the automotive industry. They performed several tests to characterize the mechanical properties of the
micro-systems. Their results show an improved hardness and cross-sectional uniformity for the MEMS parts. Recently, Doroftei et al. [42] used a unique self-combustion method with the sol-gel technique to produce NC SrMnO$_3$, a perovskite-type oxide compound, for capacitive and/or resistive humidity sensor applications with an average crystallite size of 88.9 nm. They were able to produce samples with a porous grain structure and good crystallinity.

Over the past two decades, a lot of research has been done to develop NC materials and their processing techniques to improve their mechanical properties. However, there are a few challenges as well. The first issue that may be encountered during the cryomilling process is to avoid the contamination of metal powders [101]. This issue is yet to be addressed by researchers. Apart from this process-specific issue, there is one more common issue with the NC structures. Any processing route for producing NC material requires material to be post-processed. During this post-processing, the grain boundaries of NC materials are often prone to nucleation and grain growth during the application of heat due to grain boundary relaxation and grain aggregation. Restricting this grain growth is an active challenge that researchers have been facing. Achieving the thermal stability of NC grain boundaries is vital in maintaining the characteristic superior properties of NC materials. This is essential for implementing the usage of NC materials in vivid commercial production processes and applications [146]. Recent studies suggest using a slow cooling rate could help avoid grain growth during post-processing stages [147].

According to the Hall-Petch relation, the strength of the material tends to increase with the decrease in the grain size. However, it is also important to note that once the
grain size is reduced below a specific critical value, the material becomes softer as per the inverse Hall-Petch relation. The mechanical properties can easily be altered by limiting the grain size by either controlling the process parameters or introducing a second phase to restrict the growth and shrinkage of the grain boundaries. Recent studies suggest that doping the matrix grain boundary with a secondary element can restrict grain growth due to the Zener pinning effect [12]. NC materials have a lot of potentials, and thus much research is being conducted in this area. In the future, the focus should be on improving NC materials’ ductility since the ductility of NC materials is inherently limited [50]. The field of NC materials is proliferating, and hence, scholars may also look for its novel prospective applications in other unexplored fields.

6. Conclusions

In this review article, a comprehensive discussion on bulk-nanostructuring of metals and alloys was elucidated. Various methods of bulk-nanostructuring, such as rapid solidification, chemical precipitation, chemical vapor deposition, and mechanical alloying, including HEBM, and cryomilling were discussed in detail. Nanostructuring of a broad spectrum of engineering materials, such as titanium, aluminum, nickel, iron, and their alloys synthesized using different techniques was explained. This article emphasizes on cryomilling synthesis method and demonstrates features and benefits over other processing methods. The effects of the cryomilling process on the microstructural features and mechanical properties of bulk-nanostructured powders were explained. The problem of grain growth and recovery is highlighted. Another critical issue is the risk of powders contamination from the milling media during the cryomilling process. Owing to its excellent properties, NC materials surely have many potential applications, which need to be explored thoroughly in the near future. This review article can offer better insights in understanding different synthesis methods and choosing appropriate process parameters to produce bulk NC materials with superior mechanical properties.

Author Contributions: Conceptualization, A.K.K.; methodology, A.K.K. and M.J.; writing—original draft preparation, A.K.K. and M.J; writing—review and editing A.K.K., M.J. and P.L.M.; supervision, M.M. and P.L.M.; funding acquisition, M.M. and P.L.M. All authors have read and agreed to the published version of the manuscript.

Funding: The authors acknowledge the financial support from the US Department of Energy (DOE) within project number DEEE0009116.

Data Availability Statement: Not applicable.

Acknowledgments: The authors acknowledge the Department of Mechanical Engineering, University of Nevada, Reno, for providing all research facilities.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

Abbreviations

| Abbreviation | Description                                      |
|--------------|--------------------------------------------------|
| BCM          | Biomorphic carbon materials                      |
| CC           | Cold compaction                                  |
| CCVD         | Catalytic chemical vapor deposition              |
| CNT          | Carbon nanotubes                                 |
| CoF          | Coefficient of friction                          |
| CPP          | Cyclic potentiodynamic polarization              |
| EPD          | Electrophoretic deposition                       |
| FCC          | Face centered cubic                              |
HA Hydroxyapatite
HF Hydrofluoric acid
HIP Hot isostatic pressing
HEBM High energy ball milling
HNO₃ Nitric acid
HT High temperature
MA Mechanical alloying
MEMS Microelectromechanical systems
MC Microcrystalline
NC Nanocrystalline
PECVD Plasma enhanced chemical vapor deposition
RE Rare earth
RPM Rotations per minute
RT Room temperature
SEM Scanning electron microscopy
SPS Spark plasma sintering
SLM Selective laser melting
SPD Severe plastic deformation
SS Stainless steel
TEM Transmission electron microscopy
UTS Ultimate tensile stress
UFC Ultra-fine crystalline
UFG Ultra-fine grains

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