Video Article

Processing of Bulk Nanocrystalline Metals at the US Army Research Laboratory

Vincent H. Hammond¹, Billy C. Hornbuckle¹, Anit K. Giri¹, Anthony J. Roberts¹, Thomas L. Luckenbaugh², Joseph M. Marsico³, Scott M. Grendahl¹, Kristopher A. Darling¹

¹Weapons and Materials Research Directorate, US Army Research Laboratory

²Bowhead Total Enterprise Solutions, LLC

³Oak Ridge Institute for Science and Education

Correspondence to: Kristopher A. Darling at kristopher.a.darling.civ@mail.mil

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Abstract

Given their potential for significant property improvements relative to their large grained counterparts, much work has been devoted to the continued development of nanocrystalline metals. Despite these efforts, the transition of these materials from the lab bench to actual applications has been blocked by the inability to produce large scale parts that retain the desired nanocrystalline microstructures. Following the development of a method proven to stabilize the nanosized grain structure to temperatures approaching that of the melting point for the given metal, the US Army Research Laboratory (ARL) has progressed to the next stage in the development of these materials - namely the production of large scale parts suitable for testing and evaluation in a range of relevant test environments. This report provides a broad overview of the ongoing efforts in the processing, characterization, and consolidation of these materials at ARL. In particular, focus is placed on the methodology used for producing the nanocrystalline metal powders, in both small and large-scale amounts, that are at the center of ongoing research efforts.

Video Link

The video component of this article can be found at <https://www.jove.com/video/56950/>

Introduction

Nanocrystalline metals prepared by high energy mechanical alloying have been shown to exhibit superior mechanical strength as compared to their coarse-grained counterparts. However, as dictated by thermodynamic principles, nanocrystalline microstructures are subject to grain coarsening at elevated temperatures. As such, processing and applications of these materials is currently limited by the ability to create stabilized microstructures in bulk form. Given the potential of these materials, two primary methods are being pursued in an effort to develop such systems. The first, based on a kinetic approach, utilizes several mechanisms to apply a pinning force on the grain boundaries (GBs) in order to prevent grain growth. Typical mechanisms employed to pin the GBs are secondary phases (Zener pinning)^{1,2,3} and/or solute drag effects^{4,5}. The second method, based on a thermodynamics approach, suppresses grain growth by reducing the GB free energy through solute atoms partitioning to the GBs^{6,7,8,9,10,11,12,13,14,15,16}.

As the first step to developing alloys with a nanograined microstructure, the fundamental understanding into thermodynamic and kinetic principles that govern grain growth and microstructural stability at elevated temperatures was established. Computational materials science was also used to guide alloy development. Using these insights, small scale lots of various alloy powders were produced using high energy milling and evaluated for a broad range of physical and mechanical properties. For the more promising systems, advanced characterization techniques were developed in order to fully link the microstructure of the powder to the observed properties and performance.

Simultaneously, the infrastructure and equipment needed to produce bulk components from the nanocrystalline powders was acquired. Once this equipment was in place, the processing science required to fully consolidate bulk materials from the alloy powders was developed through a series of small scale experiments. Once bulk specimens were available, a series of experiments were performed to understand the mechanical response of these materials under a broad range of conditions (such as fatigue, creep, high strain rate, etc.). The knowledge gained from these experiments has been used to develop possible application spaces that will enable the commercialization of the stabilized bulk nanocrystalline alloys.

Collectively, meeting these tasks has led to the development within the U.S. Army Research Laboratory (ARL) of a nanocrystalline metals research center consisting of 4 main labs. This laboratory complex represents a total investment of 20 million USD and is unique in that it spans aspects of fundamental, applied, and manufacturing science. The primary purpose of these labs is to transition proof-of-concept ideas to the pilot-scale and pre-manufacturing levels. In doing so, it is anticipated that the labs will enable the production of prototype parts, develop the

necessary know-how and manufacturing science for scaled-up processing, and allow for linkages internally as well as to external research institutes or industrial partners via the commercialization and transition of this advanced powder technology.

As indicated earlier, the first step is to identify, produce, and rapidly assess new alloy prototypes for both feasibility of synthesis and fabrication into prototype parts. To accomplish this, several unique, custom-designed high energy shaker mills have been constructed with the capability to process powders over a wide range of temperatures from -196 °C to 200 °C. As the name implies, these mills produce approximately 10-20 g of fine powders through the violent shaking action that causes repetitive impacts between powder and grinding media to produce powders in which each particle has a composition in proportion to the starting elemental powder mix. While suitable for the rapid screening of powders, mills of this type are clearly not suitable for powder production on the (near) industrial scale (e.g., kilograms).

Given the need to produce powder in large quantities and in as continuous a process as possible, a search was undertaken to identify potentially viable methods and equipment. Planetary ball mills use a support disk which rotates in the opposite direction from the vertically oriented vials, resulting in particle size reduction due to both grinding and collisions caused by centrifugal forces. Lot sizes for most planetary mills range up to approximately 2 kg. Unlike conventional mills, attritor mills consists of a series of impellers inside a vertical drum. The rotation of the impellers cause the motion of the grinding media, resulting in particle size reduction through collisions between powder, balls, and the impellers. Larger attritor mills are capable of producing over 200 kg per run. Although both of these mills offer significant increases in lot sizes relative to shaker mills, they are not capable of running in a continuous fashion but must rather be loaded and unloaded manually for each run.

Due to these shortcomings, attention shifted to a series of high energy, horizontal rotary ball mills. Capable of processing as much as 200 kg per batch, these mills are also capable of operating under inert atmospheres as well as vacuum. Finally, the milling chamber has been designed with an airtight that allows for the rapid and automated removal of powder once the milling process has been completed. Combined with an automatic powder injection system, this means that the ball mill is capable of running in a fairly continuous manner, thereby making it a highly viable system for industrial settings. Due to these combination of features, ARL has recently purchased and installed two mills and is now engaged in upscaling internal powder processing efforts.

While the powder processing efforts represent a central aspect of on-going efforts, the characterization and consolidation of the most promising alloy powders are also areas of focused research. Indeed, as detailed below, ARL has made notable investments in the requisite analytical and test equipment needed to fully evaluate key features of the new powders. Moreover, successful consolidation of samples now allows for conventional full scale mechanical testing and characterization (e.g., tension, fatigue, creep, shock and ballistic evaluation) of these materials which has typically not been feasible for this class of material. This article reports the protocols utilized at ARL for initial synthesis, scale-up, consolidation and characterization of bulk nanocrystalline metals and alloys.

The two main labs for powder synthesis can be seen in **Figure 1**. **Figure 1A** shows the small-scale powder processing lab which enables the rapid development of concepts and alloy design. This lab contains several custom-designed high energy mills with the capability to process powders over a range of temperatures (room temperature to 400 °C and 10 to -196 °C). The lab also contains a custom horizontal tube furnace designed for the rapid assessment of the thermal and microstructural stability (e.g., grain growth studies) of new metal alloys. Finally, the lab also houses several unique small-scale mechanical test setups including tension, shear punch, and impression creep testing devices, as well as a state-of-the-art instrumented nano-indenter. Once thoroughly tested and of shown promise, selected alloys are moved to the large scale processing lab (**Figure 1B**), where the engineering and manufacturing protocols are developed to allow large scale (e.g., kilogram) production of the specific powder. In total, the labs represent a total investment on the order of 2 million USD and covers the transition of novel metal powders from the lab bench to the pilot-scale manufacturing levels, thereby enabling the production of prototype parts.

High energy ball milling/mechanical alloying is a versatile process for producing nanocrystalline metals and alloys in powder form¹⁷. Starting with coarse grained powders (typically mean grain size ~5-10 µm), it is possible to obtain nanocrystalline powders with mean grain size < 100 nm after milling. This milling is routinely performed in a vibratory/shaker mill. The milling vial is filled with the desired amount of powder as well as milling balls, typically stainless steel. This mill shakes the vials in a motion that involves back and forth oscillations with short lateral movements at a rate of approximately 1080 cycles min⁻¹. With each complex motion the balls collide with one another, impact against the inside of the vial and the lid, and simultaneously reduce the powder to finer size. The kinetic energy imparted into the powder is equal to half the mass times the square of the average velocity (19 m s⁻¹) of the bearings. The mill power, e.g. the energy delivered per unit time, increases with the frequency of the mill (15-26 Hz). Taking the typical number of balls and the lowest frequency for a given 20 h period, the total number of impacts exceeds 1.5 billion. During these impacts the powder undergoes repeated fracturing and cold-welding until the point where the constituents are mixed at the atomic level. Microscopically this mixing and refinement of the microstructure is facilitated by localized deformation in the form of shear bands as well as a high density of dislocations and point defects which breaks down the microstructure. Eventually, as the heat of collision raises the local temperature, recombination and annihilation of these defects occurs at a steady state with their generation. The defect structures eventually, though reorganization, result in the formation of smaller and smaller high angle equiaxed grains. Thus, ball milling is a process that induces severe plastic deformation manifested by the presence of a high density of defects. This process allows for increased diffusivity of solute elements and the refinement and dispersion of secondary phases and the overall nanostructuring of the microstructure.

High energy cryomilling is a milling process similar to high energy ball milling except for the fact that the milling vial is maintained at cryogenic temperature during the milling process. In order to achieve a uniform temperature in the vial, the mill has been modified as follows. The milling vial is first placed inside a Teflon sleeve which is then sealed with a Teflon cap. The sleeve is connected to a dewar containing the appropriate cryogen (liquid nitrogen (LN₂) or liquid argon (LAr)) through stainless steel and plastic tubing. The cryogen flows through the sleeve throughout the milling process to cool the milling vial and maintain the milling vial at the boiling temperature of the cryogen, such as -196 °C for LN₂ and -186 °C for LAr. The low temperatures of cryogenic processing lead to the increased fragmentation of more ductile metals which otherwise cannot be milled at room temperature. Additionally, the cryogenic temperatures reduce thermally activated diffusional processes such as grain growth and phase separation thereby allowing increased refinement of the microstructure and solubility of insoluble elemental species.

The high energy horizontal rotary ball mill is a high energy milling system that consists of a horizontal stainless-steel milling jar with a high-speed rotor with several blades fixed on a drive shaft. The powder to be milled is transferred inside the jar along with the milling balls. Movement of the balls and powder is achieved through the rotation of the shaft inside the jar. The shaft rotates at high speed and the milling steel balls collide, accelerate, and transfer their kinetic energy to the powders. The range of rpm is 100 - 1000 and the average velocity of the balls is 14 m s⁻¹.

In particular, mills are equipped to operate over a range of milling temperature ($-30\text{ }^{\circ}\text{C}$ to $200\text{ }^{\circ}\text{C}$ high) and can be run under vacuum (mTorr) or in over pressure mode (1500 Torr) (utilizing various types of cover gas). In addition to the base unit, the mill is equipped with a carrier gas discharge unit as well as connection assemblies which allows the loading and unloading of powder under inert gas cover. This apparatus can be seen in **Figure 2A** along with a typical 8 L steel milling jar (**Figure 2B**). In addition to the larger mill, ARL has purchased a smaller mill which has been converted to run under liquid nitrogen (**Figure 2C**). This mill can produce between 100-400 g of processed powder per running cycle.

Protocol

1. Small Scale Synthesis of Nanocrystalline Powders under Ambient Conditions

1. In a controlled argon atmosphere glove box, place 10 g of the primary element (e.g., Fe in FeNiZr alloy) and 100 g of stainless steel/tool steel milling balls in the desired milling jar.
NOTE: Loading of powder into milling jar inside a glove box is required to ensure minimal uptake in oxygen and/or moisture content^{18,19}.
2. After loading, seal the jar and remove from the glove box. After removal, ensure that jar is fully sealed and load into the appropriate milling machine.
3. After performing a 1 h milling cycle, remove the vial and transfer it back into the argon-filled glove box.
NOTE: This short run serves to coat all surfaces with the primary element, thereby helping to reduce the transfer of contaminants from milling jar and media to the alloy being produced.
4. To synthesize the alloy powders, add a total of 10 g of elemental powders in the desired ratios to the just coated milling jar inside the glove box. Add the required amount of just coated milling balls to the jar such that there is a 10:1 ratio of the mass of the balls to mass of powder. The lid should be placed and tightened on the milling jar before removal from the glove box. After removal, further tightening of the lid should be performed using a wrench and a vice.
5. Place the vial in the high energy shaker mill and initiate milling operation (typically on order of 20 h). After the milling is completed, remove the vial and transfer it to the glove box. Carefully remove the lid and transfer the milled powder to the desired sample vial for storage.
NOTE: A typical high energy shaker mill used in mechanical alloying is shown in **Figure 3A**. A schematic showing how high energy milling results in nanocrystalline materials is shown in **Figure 3B**, with an image showing an average final particle size between 10 and 500 μm shown in **Figure 3C**.

2. Small Scale Synthesis of Nanocrystalline Powders under Cryogenic Conditions

1. Perform coating run for milling jar and balls as described in Steps 1.1-1.3.
2. In controlled atmosphere glove box, fill coated milling jar with desired amount of elemental powders and milling media. After tightening the jar, remove from the glove box.
3. Place the milling jar inside a Teflon sleeve and cap, which is then placed in the clamp of the high energy shaker mill.
4. Open the dewar containing the cryogen and allow it flow for about 30 min to ensure the milling jar has reached the desired temperature ($-196\text{ }^{\circ}\text{C}$ for liquid nitrogen and $-186\text{ }^{\circ}\text{C}$ for liquid argon).
5. Upon reaching equilibrium, initiate the milling operation until the desired duration has been reached. Upon completion, close the dewar, carefully remove the milling jar from the sleeve and place it in front of a dryer to bring it to room temperature.
6. Once the milling jar reaches room temperature, transfer it back inside the controlled atmosphere glove box. Carefully open the milling jar and transfer the powders to desired storage vial.
NOTE: A picture of the high energy shaker mill adapted for use at cryogenic temperatures is shown in **Figure 4A**. Shown in **Figure 4B** is a milling vial immediately after it has been removed from a cryomilling operation. **Figure 4C** provides an idea of the number of milling balls typically used in a processing operation.

3. Large Scale Synthesis of Nanocrystalline Powders

1. Load the required elemental alloying powders into a glass jar inside an argon glove box, seal, and remove.
2. After attaching the vessel to the high-energy horizontal rotary ball mill, load approximately 1 kg of 440C stainless steel ball bearings into a stainless steel 8 L vessel contained within a cooling jacket.
Note: Images of the various parts of the high energy horizontal rotary ball mill are shown in **Figure 5**.
3. Connect the argon gas line and coolant lines to the vessel. Back-fill and purge the vessel with argon gas to remove air.
4. Using a double ball valve, transfer the alloying elemental powders into the milling vessel and then close the valve to seal the chamber.
5. Connect the powder extraction system to the milling vessel and then back-fill and purge the extraction system with argon gas to remove air.
6. Start flowing ethylene glycol at $-25\text{ }^{\circ}\text{C}$ through the outer jacket of the vessel.
7. Begin the milling process for up to 1 kg of elemental powders for the desired amount of time (typically 12-30 h) using rotational energy of 400-800 rpm. Once the milling is completed, transfer the powders to a jar under argon atmosphere. Store the jar in an argon filled glove box.

Representative Results

Approximately 10 g of powder are produced per each run in the high energy shaker mill. After successful synthesis of novel nanocrystalline metals and alloys in high energy shaker mill, scale-up is conducted in a high energy horizontal rotary ball mill.

Typically, nanostructured powders are generated using high energy milling processes, wherein the grain size of a small amount of powder is refined, approximately 10 g per batch. This is satisfactory on a small proof-of-concept scale. However, there exists a need for larger milling apparatuses that can do the same but producing larger quantities. Significant quantities of powders allow for the production of bulk parts that, in turn, can be tested at a relevant size scale appropriate for Army specific applications.

On a small 5 to 10 g scale, the energy imparted to a coarse powder may be achieved with relative ease in a small-scale research laboratory shaker mill. The translational energy imparted by the balls causes the breakdown of the particles resulting in an ultrafine grained powder mass. The scaling of this methodology from gram size to kilogram (1000 g) batches entails the dimensional scaling of the milling jars and associated apparatus, which is complex because, at the same time, the imparted energy needs to be scaled as well. In this context, the high energy horizontal rotary ball mill can create the unique nano-scale sub structural features (*e.g.*, short and long range ordered structures, point defects, atomic clusters, stacking faults, precipitates, dispersions, amorphous features) that impart these materials with the dramatic improvement in properties in an acceptable time frame with minimal contamination^{20,21}.

In a two element component system, **Figure 6**, the milling process results in a series of repeated impacts that cause the powder particles to "cold" weld together via plastic deformation, fracture, and then reweld throughout the duration of the milling. As a result, a variety of final microstructures are possible: 1) a nanocrystalline matrix with grain boundary segregated atoms of the secondary phase, 2) a supersaturated solid solution of both components, 3) a nanocrystalline matrix with grain boundary segregated atoms of the secondary phase coexisting with a supersaturated solid solution of the two, 4) a nanostructured composite of the two distinct phases, 5) a super saturated solid solution with large dispersions of the second phase and 6) a combination including all of the above. In general though, the microstructure is nanocrystalline with an average powder particle size between 10 and 500 μm (**Figure 3C**). It is important to note that the final particle size depends heavily on the milling temperature, time, energy and physical characteristics/properties of the individual constituents. The average grain size produced typically scales inversely with the melting temperature of the alloy but does depend on the milling conditions and the extent of alloying produced. The typical average grain size produced by high energy milling is less than 50 nm. However, the minimum grain size attained can be below 5 nm or even in some cases the amorphous limit can be reached. As a result of the small grain size, there exists a significant volume fraction of grain boundaries and triple junctions. Therefore, nanocrystalline metals and alloys have altered physical responses to temperature and deformation. That is, metals have problems pertaining to thermal stability which limits processing techniques as well as applications to moderate and sometimes low temperatures. These hurdles can be overcome by manipulation of the interface between the nanocrystalline grains through doping with solutes. As mentioned above, the dopant can take the form of segregated solute or discrete particles or a combination thereof and can halt grain growth even at very high temperatures, thereby allowing full consolidation through high temperature forging without loss of the advantageous mechanical properties.

The initial step in characterizing the mechanically alloyed powders is observing the loose powder morphology using a Scanning Electron Microscope (SEM). This step is performed to determine if the individual particles composing the powder show a distinct change in morphology, *e.g.*, from a plate-like morphology at short milling times to a more spherical shape after extended milling times. Next, a small amount of the as-milled powder is pressed at 3 GPa into 3 mm green compacts which are subsequently mounted in epoxy and polished. The polishing steps utilized are sample dependent. However, a final polishing step of 1 μm or finer is required to achieve the needed surface finish for SEM observation. By polishing the compacts to a final polish of one micron, back-scattered electron images can be taken that show the distribution of the solute elements as a function of milling time. Imaging using back-scattered electron is the preferred technique since the contrast is based on atomic number. As a result, areas with higher amounts of the heavier element in an alloy show up brighter. These images as well as X-ray diffraction data can provide insight as to when the solute fully enters into solid solution as well as the maximum amount of solute that can be put into solid solution.

In general, the individual grains are too fine to resolve using just the SEM. Consequently, Transmission Electron Microscopy (TEM) is required to resolve the individual grains within a mechanically alloyed powder. TEM sample preparation depends upon whether the alloyed powder has been consolidated into a dense, bulk sample or not. If the powder is not a consolidated bulk sample, a dual beam focused ion beam (FIB) / scanning electron microscope (SEM) is used to lift-out and thin a lamella of the specimen to electron transparency²². The lamella can be taken from a single, loose particle or from a polished SEM (3mm compact) specimen where the cross section of individual particles are exposed. For bulk specimens, a 3 mm diameter disc is punched out using a disc punch. The 3 mm disc is then ground down to approximately 100 μm . Next, a dimple grinder is used to create a dimple within the center of the disc. Ideally, the thickness at the bottom of the dimple is less than 10 μm . Once the desired dimple depth is achieved, the sample is ion milled until electron transparent.

The TEM analysis is performed at 200 keV using a microscope equipped with scanning transmission electron microscope ((S)TEM) capabilities. The authors have utilized both standard TEM and STEM-based imaging technique depending upon the microstructural features being investigated. With that said, the authors have found STEM bright field and STEM-High Angle Annular Dark Field (HAADF) as two extremely powerful techniques. STEM bright field has been utilized with tremendous success at imaging/resolving grains over large areas of a sample while simultaneously highlighting the presence of particles/clusters and twins. The contrast generated in a STEM-HAADF image is based on z-contrast, *i.e.* atomic number of elements present in a sample, which is a powerful way to gain insight into the relative chemistry of varying microstructural features. **Figure 7A** is a STEM bright field image of a Cu-10Ta (at.%) sample equal channel angular extruded (ECAE) at 900 °C allowing for the grains to be clearly resolved over roughly 1.5 μm^2 area. Within this image, roughly fifty grains can be measured for their grain size. Thus, taking several images of equivalent magnification allows for grain size statistics to be determined and histograms generated. **Figure 7B** is a STEM-HAADF image taken from the same area of the sample and clearly distinguishes the high number density of Ta particles present as well as the wide range of their sizes. This image can be used in a similar manner as the bright-field image, but this time to measure the Ta particle size allowing for a histogram highlighting the particle size distribution to be generated. **Figures 7C** and **Figures 7D** are STEM bright field and HAADF images taken of a Cu-10Ta (at.%) sample ECAE processed at 700 °C showing a larger Ta particle (~ 40 nm diameter) surrounded by numerous other Ta particles ranging in diameter from roughly 5 to 20 nm. The larger Ta particle also has a unique microstructural feature present with a partial shell formed around its lower half.

Atom probe tomography (APT) analysis is then performed to further understand the key features of the powder (**Figure 8A**). **Figure 8B** shows the two viewing ports used for maneuvering samples from the staging carousel to the analysis chamber. **Figure 8C** shows both the load lock and buffer chamber with the gate valve separating the two chambers in the atom probe system. The load lock is where new samples are loaded and old samples are removed. The buffer chamber houses samples that are awaiting examination in the analysis chamber.

Before atom probe samples/tips can be placed in the chamber, the tips are lifted-out onto prefabricated Si post then annularly milled using a dual beam SEM/FIB. The ion column is generally operated at a beam current of 30 keV during the whole procedure and only dropped to 5 keV in the final clean-up step to minimize Ga ion implantation within the final tip before performing the analysis. The beam current used varies widely depending upon the ease with which the material mills. The authors have utilized both voltage and laser mode for running different nanocrystalline-based material systems. Voltage mode is used when a specimen is highly conductive and has a low propensity for fracturing during running, while laser mode is employed for non-conductive materials and/or those specimens with a high propensity to fracture in voltage mode. The collected atom probe data is then analyzed using an appropriate software package. The atom probe has been employed to quantify the high number density of Ta particles present in Cu-10Ta²³, which are key to the outstanding properties of this material at elevated temperatures²⁴. Additionally, in ongoing research, this tool has identified the presence of WO₂ particles in electroplated NiW alloy (**Figure 9A**). **Figure 9B** shows the presence of Na particles within the atom probe tip. **Figure 9C** shows the WO₂ and Na particles at the same time. **Figure 9D** is a mass spectrum for ions with a mass to charge state ratio from 0 to 19 Daltons (Da). Identifying and quantifying segregation of both the WO₂ and Na particles to this level is not possible via any other analysis technique. Thus, characterization using SEM, TEM, and APT are essential in fully understanding the microstructure and mechanisms at play in mechanically alloyed nanocrystalline powders.

Once the thermal stability and strength of the nanosized powders were fully appreciated, it became apparent that a conventional powder processing method such as uniaxial pressing and sintering, while feasible, was not a preferred method. A method that offered the combination of temperature and an applied shear stress was needed to assure full densification of the powder compacts. As a result, the use of equal channel angular extrusion (ECAE) as a processing method was explored. In this method, a billet - in either bar or plate form - is subjected to a pure state of shear as it extruded through an L-shaped channel^{25,26,27}. As the billet does not experience a significant change in dimensions during the extrusion process, it can be subjected to multiple passes until the desired amount of shear (and by extension microstructural refinement) has been imparted. Finally, the billet can be rotated between each pass in order to generate the desired degree of texture in the final part. As a result, it is possible to achieve a final extrudate with a significantly refined microstructure and desired texture. A schematic and a partially extruded billet which shows the dramatic change in grain size and orientation in the extruded portion relative to the non-processed part are shown in **Figure 10A** and **Figure 10B**, respectively.

The US Army Research Laboratory has actively used ECAE processing in numerous efforts over the last decade. The press is capable of processing billets at a rate as high as 2.5 cm s⁻¹ under a maximum applied load of 345 t, with a maximum die temperature of 350 °C (**Figure 11A**). Samples requiring a higher processing temperature are preheated in a box furnace located adjacent to the frame. After the desired pre-heating regime is completed, the sample is rapidly transferred to the die and the extrusion immediately started. The initial ECAE press capability focused on rectangular billets on the order of 1.91 cm square × 22.8 cm long (**Figure 11B**). Continued upgrades in capabilities has resulted in the ability to process 15×15×1.27 cm³ as well as 30×30×2.5 cm³ plates.

Of more import for this discussion, however, is the fact that ECAE is routinely used to consolidate a broad range of powders not readily consolidated by other means^{28,29,30}. In the approach adopted at ARL, the desired amount of as-milled powder is introduced into a cavity machined into a nickel rod (e.g., a "nickel can"). As the powder is introduced into the cavity, it is routinely tapped in order to minimize any filling induced porosity. Once the desired amount of powder is added, the opening is plugged and then welded shut. It is important to note that the "powder canning" process is conducted inside an argon filled glove box in order to minimize the introduction of oxygen. To date, this process has been used to prepare "cans" of both Cu-Ta and oxide dispersion strengthened (ODS) FeNiZr alloy powders, with the exact protocols described below.

Starting in 2011, a series of nanocrystalline (e.g., Cu-Ta, FeNiZr) alloys that showed remarkable grain growth resistance and thermal stability have been developed at ARL^{12,18,19,31,32}. As it became apparent that conventional press and sinter processing methods were not suitable, ECAE became the primary means for consolidating small samples suitable for testing. As a first step in ECAE processing, the nickel cans loaded with as-milled powders were equilibrated in a box furnace purged with pure Ar gas at a pre-determined temperature (e.g. 700 °C). The equilibrated cans were then quickly removed from the furnace, dropped into the ECAE tooling pre-heated to the desired temperature and extruded at an extrusion rate of 25.5 mm s⁻¹. This procedure was repeated four times following route Bc (defined as 90° rotation in same direction between passes³³). The four consecutive extrusion passes resulted in a total strain of ~450%. Scanning electron microscopy indicated that the samples were fully consolidated with no evidence of porosity or prior particle boundaries. Further, grain size measurements indicated no appreciable grain growth occurred during the ECAE processing.

Recent processing efforts have focused on upscaling the size of parts produced from the FeNiZr nanocrystalline alloy powders. The initial attempt at upscaling used Hot Isostatic Pressing (HIP). In this attempt, as-milled FeNiZr powder was loaded in approximate 10 g lots into an open-ended aluminum can located inside an inert atmosphere glovebox. Following each addition of powder, the powder load in the can was compressed using a manually actuated hydraulic press to approximately 50 kN of force. Prior to sealing the can, it was heated inside an oven at approximately 200 °C for 24 h. A vacuum pump was attached in order to pull out any moisture from inside the can. The can was then welded shut (**Figure 12A**) and placed inside the HIP unit (**Figure 12B**) for processing. Hot Isostatic Pressing was performed on a range of samples at temperatures ranging from 600-1000 °C and a pressure of 207 MPa. However, regardless of the temperature used, all samples displayed a maximum density of ~96%.

Since HIP was not capable of producing fully dense samples, further efforts were performed using a conventional extrusion press. For this approach, aluminum cans measuring approximately 7.5 cm in diameter by 11 cm in height were packed with Fe-Ni-Zr powder in a manner similar to the smaller samples described previously. Prior to the actual extrusion, the extrusion chamber, die holder, and die were heated to temperatures ranging from 400 to 450 °C. Once the billet reached an equilibrium temperature of 1000 °C, it was quickly pulled from the furnace and loaded into the heating chamber of the extruder. After loading, the billet was extruded at approximately 1 cm s⁻¹ using ratios of 2:1 and 3:1. For safety and practical reasons, the billets were not fully pushed through the extrusion die. After the completion of a full extrusion cycle, the dies were removed from the die-holder while still hot, then allowed to cool. Wire electrical discharge machining (EDM) was then used to cut the dies away from the extruded billets. The higher temperature of 1000 °C allowed for a successful extrusion (**Figure 12C**). Further extrusions are planned, with the intent of optimizing processing parameters and material properties based upon a detailed analysis on the extruded billets.

In an effort to develop advanced materials capable of meeting the performance requirements dictated by unique operational environments, the US Army Research Laboratory has devoted significant resources to establishing a nanocrystalline metals research center. As briefly detailed in this report, the lab consists of an array of equipment and expertise devoted to the processing and characterization of novel metal powders, as well as the subsequent consolidation and performance evaluation of bulk nanocrystalline parts. Current efforts in Cu-Ta and FeNiZr alloys have demonstrated the ability to successfully transition from small scale research efforts to larger programs which have allowed for the "full-scale" testing of these materials in a variety of conditions (e.g., tension, fatigue, creep, shock, and ballistic evaluation) that has not previously been readily accomplished. Future efforts will focus on the transition of these exciting materials to a range of actual components, as well as the continued development of new alloy systems.

Figure 1: Powder Processing Labs at Army Research Lab. A) Small scale synthesis lab used for the production of small batches (10 g) of novel powders. Important equipment contained in the lab are high energy shaker mills that operate over a range of temperatures as well as specialized test equipment. B) Large scale synthesis lab in which promising alloy powders are produced in up to 1 kg batches. [Please click here to view a larger version of this figure.](#)

Figure 2: Critical components of the high energy horizontal rotary ball mill used in large scale synthesis of nanocrystalline powders. A) Carrier gas discharge unit, B) Representative 8 L milling jars, C) Small scale high energy horizontal rotary ball mill. [Please click here to view a larger version of this figure.](#)

Figure 3: Small scale powder synthesis under ambient conditions. A) Modified high energy shaker mill which can operate from -20 to 24 °C and up to 2200 cycles per minute. B) Schematic of high energy milling process to form nano-structured/nanocrystalline powders. C) Resultant powder (average particle size 40 μm *i.e.* ~ -325 mesh) having an internal grain size of 10 nm. [Please click here to view a larger version of this figure.](#)

Figure 4: Small scale cryogenic milling of nanocrystalline powders. A) Modified high energy shaker mill which can operate at cryogenic temperatures. B) Vial right after removal from cryomilling. C) Standard vial showing the number of bearings typically used. [Please click here to view a larger version of this figure.](#)

Figure 5: Hardware systems associated with large scale high energy horizontal rotary ball mill. A) Images of the larger mill. B) High-speed rotor with several blades. C) Inside surface of milling jar. [Please click here to view a larger version of this figure.](#)

Figure 6: Schematic of the milling process for two element system. Repeated collisions between milling media and powder results in a range of resulting microstructures. [Please click here to view a larger version of this figure.](#)

Figure 7: Representative microstructural features obtained through high resolution electron microscopy. A) STEM bright-field and B) STEM-HAADF images taken from the same area of the Cu-10Ta (at.%) sample ECAE processed at 900 °C; C) STEM bright-field and D) STEM-HAADF images taken from the same area of a Cu-10Ta (at.%) sample ECAE processed at 700 °C. STEM-based techniques have been vital in elucidating the microstructural features governing the outstanding mechanical properties present in CuTa alloys as well as other nanocrystalline powder based materials. [Please click here to view a larger version of this figure.](#)

Figure 8: Atom probe tomography is a valuable tool in analyzing various powders produced at ARL. A) The full atom probe tomography system. B) Enlarged image showing the two viewing ports on the buffer chamber. C) A close up of the load lock and buffer chamber. [Please click here to view a larger version of this figure.](#)

Figure 9: Representative elemental maps obtained during atom probe tomography. A) 3D atom map displaying only W (red spheres) and WO_2 (blue spheres) atoms; B) 3D atom map displaying only W (red spheres) and Na (green spheres) atoms; C) 3D atom map displaying only W (red spheres), WO_2 (blue spheres), and Na (green spheres) atoms; D) Mass spectrum showing the mass-to-charge-state ratio from 0 to 19 Da, which are the lower atomic number elements that are the most difficult to identify and quantify using other analysis techniques. [Please click here to view a larger version of this figure.](#)

Figure 10: Equal channel angular extrusion has been successfully used to produce fully dense cylinders from the alloyed powders.

A) Schematic of the ECAE process showing how grain refinement occurs as the material passes through the 90° bend in the die. B) Optical micrograph of a partially ECAE processed sample showing changes in grain structure. [Please click here to view a larger version of this figure.](#)

Figure 11: Equal Channel Angular Extrusion press currently in place at Army Research Lab. A) In its current configuration, the ECAE press is capable of processing $19 \times 19 \times 228 \text{ mm}^3$ square billets. The press also has the capability to process $152 \times 152 \times 12.7$ and $304 \times 304 \times 25.4 \text{ mm}^3$ plates. B) Close-in photograph showing how the billet is introduced into the top of the die. [Please click here to view a larger version of this figure.](#)

Figure 12: Hot isostatic pressing and extrusion are two methods commonly used to consolidate bulk samples from starting powders. A) Sealed HIP can ready for insertion into B) HIP unit. C) Partially extruded FeNiZr billets. The sample on the left is a 1:3 ratio extrusion while the billets in the center and right are a 1:2 ratio extrusion.

Discussion

Compared to other synthesis techniques, mechanical alloying is an extremely versatile method for producing metal and alloyed powders with grain sizes $\ll 100$ nm. Indeed, mechanical alloying is one of the few ways in which large volumes of nanostructured materials can be produced in a cost effective and easily scalable manner. Furthermore, high-energy ball milling has been shown to vastly increase the limit of solid solubility in many metallic systems in which equilibrium room temperature solubility does not otherwise exist. This allows for new types of alloys to be produced which is not possible with other equilibrium processing techniques.

Although not necessarily required, the proper preparation of the milling media (e.g., coating runs) is highly recommended in order to minimize the amount of contaminants introduced into the final powder. Similarly, handling of the powder, either before or after milling, should be performed in a controlled atmosphere glove box in order to minimize exposure to oxygen and/or moisture contamination. Finally, care and caution should be used in opening the milling vial after a process run, as the vial can potentially become pressurized during the milling of powders under certain operating conditions.

Modifications to the room-temperature milling of powders is often required in order to achieve the desired results. For example, cryomilling is used to reduce the ductility for selected powders in order to ensure that the particles are broken down during milling. Alternatively, a process control agent such as stearic acid can also be used to reduce particle agglomeration during milling. The use of these methods is determined on a case by case basis.

Although mechanical alloying is a viable process for most metal powders, there are some cases where its use is problematic. Specifically, mechanical alloying requires the transfer and mixing and/or blending of elements or compounds, the degree of which is highly influenced by the milling energy and milling time as well as the difference in physical properties such as hardness, ductility, and relative solubility of components. Milling energy is a parameter which can be changed within an order of magnitude or so, but beyond that is a relatively fixed quantity and therefore the degree to which compounds or solids can be formed in any given experiment can be limited based on physical and thermodynamic parameters governing mechanical properties and the solubility. Extending milling time to achieve further refinements or mixing places practical cost limits on the production of powders and must be evaluated against the performance-cost tradeoff. Additionally, increased milling times

can lead to elevated contamination via interaction of the powders with the milling media or atmosphere. Higher levels of contamination can dramatically alter physical properties and performance of the powder and/or consolidated parts.

This report has detailed the use of mechanical alloying for producing nanocrystalline metal powders suitable for both research and industrial studies. As the full potential of these materials is recognized through testing of bulk samples and/or components, they are likely to find widespread use in a variety of industrial sectors (e.g., aerospace, automotive, defense, electronics, etc.).

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