Improving the Properties of Cryomilled Light Alloys Using Spark Plasma Sintering and Hot Isostatic Pressing

Christopher Melnyk, David Grant, Steven G. Keener, Robert V. Gansert, and Steven Schroeder

Ultrafine grained materials consolidated using spark plasma sintering and hot isostatic pressing show great potential for applications in aerospace, energy, and a vast range of other industries. The Hall–Petch relationship cites the strengthening of materials by reducing the average crystallite (grain) size. A study is proposed to investigate the increase in mechanical properties provided by fine-grained, near-nano- and nano-crystalline powders produced from cryomilling and consolidation using spark plasma sintering (SPS) and hot isostatic pressing (HIPing). Initial testing indicates an increase in hardness and shear in commercially pure aluminum by 2–3 times from use of fine-grained, near-nano-, nano-crystalline materials. Cryomilled powders and consolidated forms of these powders will be examined using field emission scanning electron microscopy. Macrohardness, microhardness, tensile testing and shear testing will be performed to examine the mechanical properties.

INTRODUCTION

Fine-grained, near-nano-, and nanocrystalline materials consolidated using spark plasma sintering (SPS) and hot isostatic pressing (HIPing) show great potential for applications in aerospace, energy, and a vast range of other industries. The Hall–Petch relationship cites the strengthening of materials by reducing the average crystallite (grain) size. Fine-grain, near-nano-, and nanocrystalline materials can be produced by cryogenic milling, or cryomilling, and consolidation using HIPing and SPS. In cryomilling, these materials are produced by milling conventional feedstock materials in a cryogenic environment. Cryomilling a metallic powder in a liquid nitrogen or argon environment provides grain refinement. Cryomilling in liquid nitrogen provides the potential for forming nitrides as well. Past efforts by Boeing, Pratt & Whitney/Rocketdyne, and California Nanotechnologies, Inc., show the increase in nitrogen content in an Al-Mg-SiC based alloy as a function of the milling time. Hydrogen and carbon content remains unchanged during the milling process in a variety of aluminum-based alloys (Figure 1).

Figure 2 shows a transmission electron microscopy (TEM) image of aluminum-nitride (AlN) formed in cryomilling, with dimensions less than 10 nm.

The properties of the original (virgin) powder materials are significantly improved through the use of the cryomilling process. The grain refinement and introduction of nitrides strengthens the material considerably. As shown in an Ashby map in Figure 3, a cryomilled Al-Mg-SiC based nano-metal matrix composite (NMMC) exhibits similar specific strength and specific stiffness as that of a titanium-based alloy material. Similarly, the cryomilled Al-Mg-SiC based alloy enables a much higher service temperature than a conventional Al-Mg-SiC alloy material. Grain refinement from cryomilling in argon, without the formation of nitrides, strengthens the material considerably as well.

How would you…

…describe the overall significance of this paper?

This paper describes cryomilling aluminum, aluminum alloys, titanium, alloys and blends forming ultrafine, near-nano-, and nano-powders. Consolidating these powders with spark plasma sintering and hot isostatic pressing, and achieving improved properties over conventional materials (of the same chemistry) is also discussed.

…describe this work to a layperson?

The paper describes the formation of high strength light alloys through nano-technology processing and consolidation.

See the sidebar for experimental details.

RESULTS AND DISCUSSION

Powders

Scanning electron microscopy images of the virgin and cryomilled powders of aluminum, CP titanium, and Ti-6Al-4V are shown in Figures 4, 5, and 6.

Grain refinement along with the formation of nitrides occurs in pure aluminum and its alloys when cryomilled in nitrogen. Grain refinement along with the potential inclusion of interstitial nitrogen occurs when cryomilling titanium metals in nitrogen. Grain refinement occurs without forming nitrides or interstitial nitrogen when cryomilling in argon. In all cases, a layered structure is formed from the agglomeration (e.g., micro-welding) of the milled material with nano- and near-nano grains produced in these agglomerated layers. The agglomerated-powder particles are micron size in scale (e.g., 10–100 μm) while the grains are nano- and near-nano in size.

Hot Isostatic Pressing

The results of the cryomilled CP Ti powder that was hot isostatically pressed are hardness ($HVN_{1,000\ g}$)–393.2 transverse; 404.2 longitudinal. The average ultimate shear strength of cryomilled CP titanium was 648.3 MPa.

Table I. SPS Testing on Virgin Ti-6Al-4V and Cryomilled Ti-6Al-4V, and CP Ti Blended with 6%Al and 4%V (CP Ti-6Al-4V)

Element	Hardness (HRc)	Ultimate Tensile Strength (MPa)
Ti-6Al-4V, As Received	33.3	982.1
Ti-6Al-4V, Cryomilled, Argon	38.9	1151.8
CP Ti-6Al-4V, Cryomilled, Argon	39.8	731.1

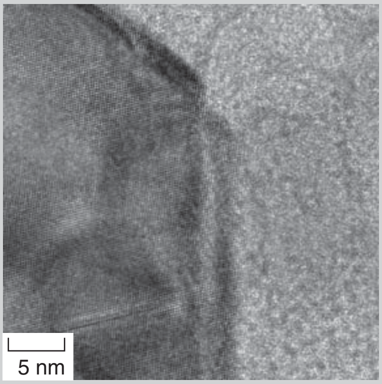


Figure 2. TEM image of aluminum nitride (AlN) formed in cryomilling of an Al-Mg-SiC based alloy.

This is greater than the tensile strength specified for CP Ti, grade 4. Commercially pure (CP) titanium, grade 4, material has a specified minimum tensile strength value of 550 MPa.

Spark Plasma Sintering

Spark plasma sintering processing was performed to consolidate virgin and cryomilled powders consisting of aluminum (series 1100), CP Ti, Ti-6Al-4V, and CP Ti blended with 6% Al and 4%V. Cross-sectioned samples of the SPS-consolidated powders exhibited excellent bonding of adjacent grains in the sintered forms for both the virgin and cryomilled materials. The mechanical properties of the SPS-processed aluminum powders are: virgin Al, series 1100: (HVN_{300g})–29.8, ultimate shear strength–129.0 MPa; cryomilled Al, series 1100: $(HVN_{300\ g})$–89.5, ultimate shear strength–266.2 MPa.

The mechanical properties of the cryomilled aluminum are improved over those of the virgin (conventional) material in the consolidated forms. In series 1100 aluminum, the strength and hardness of the cryomilled material increased with the grain refinement and the addition of nitrides. The hardness of the cryomilled aluminum was 3.0 times greater than the virgin aluminum, and the shear strength of the cryomilled aluminum was 2.1 times greater than that of the virgin aluminum.

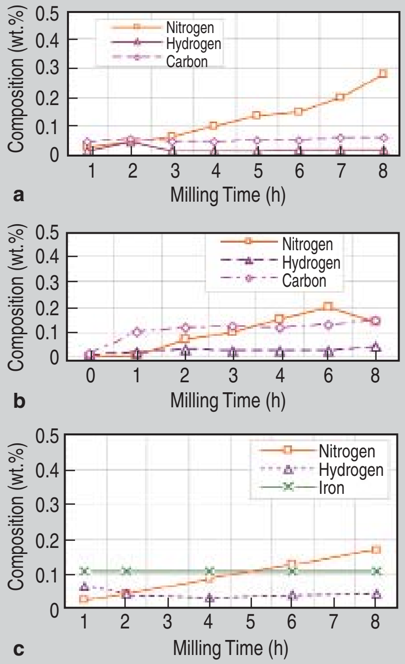


Figure 1. Nitrogen wt.% vs. milling time. (a) Al-Ti-Cu powder chemistry, (b) Al-Mg-N powder chemistry, (c) Al-Mg-N-SiC powder chemistry.

The mechanical properties of the SPS-consolidated titanium powders are provided in Table I. The mechanical properties of titanium alloys and powder blends cryomilled in argon show considerable improvement over that of virgin material in the consolidated form.

The Ti-6Al-4V increased in hardness from a value of 33.3 HRc in the virgin material, to 38.9 HRc in the cryomilled material. The strength increased from a value of 982.2 MPa in the virgin material to 1151.8 MPa in the cryomilled, high temperature vacuum degassing, and SPS-consolidated material. The CP titanium cryomilled with 6% aluminum and 4% vanadium elemental powders also showed an increase in strength from the values typically reported for commercially pure titanium, achieving a hardness of 39.8 HRc and a tensile strength of 731.1 MPa. These mechanical property improvements were provided by cryomilling in argon. The increase in properties is associated with the changes in the microstructure (e.g., grain size) as a result of the processing, as shown in Figures 7 and 8.

Cryomilling and SPS consolidating the commercially pure titanium, Ti-6Al-4V alloy, and CP titanium blended with the 6% aluminum and 4% vanadium, resulted in producing materials with reduced grain sizes. The improvements in hardness and strength are related to this grain size reduction.

For ductile polycrystalline materials, the empirical Hall–Petch equation[1,2] has been found to express the grain-size dependence of flow stress at any plastic strain out to ductile fracture. This relationship is used to predict the grain size–yield strength relationship for large-grained materials (d>100 nm) and is limited to relatively strain-free

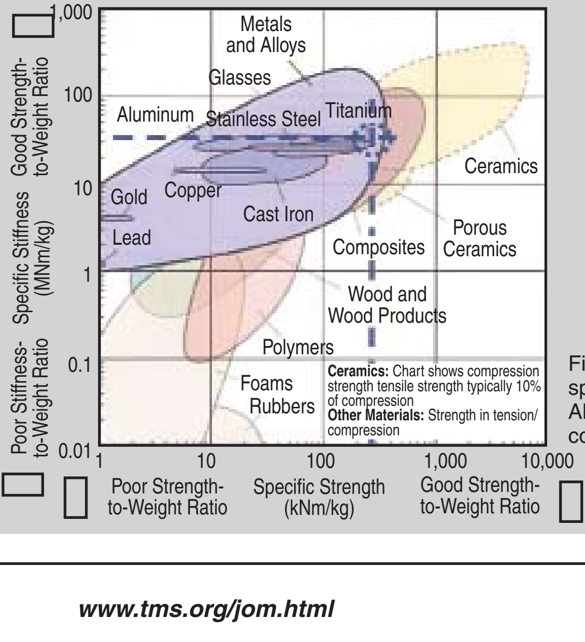
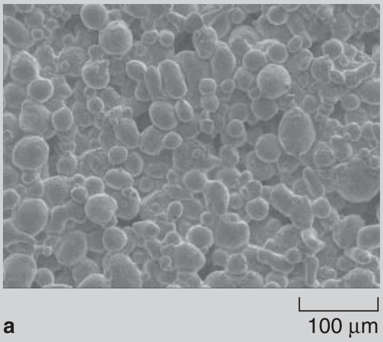


Figure 3. Specific strength and specific stiffness of a cryomilled Al-Mg-SiC nano-metal matrix composite (NMMC).

materials, predicting that the yield point will increase linearly with the inverse square root of the grain size. In terms of yield stress, the expression for this relationship is shown below. Similar results have been obtained for material hardness, with a similar relationship being also shown below. In both relationships, the Hall–Petch effect is due



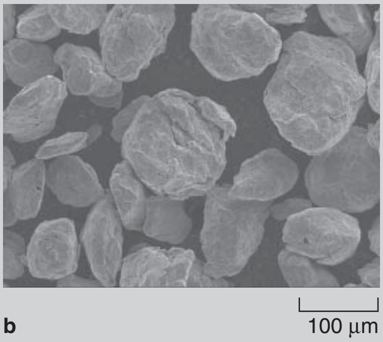
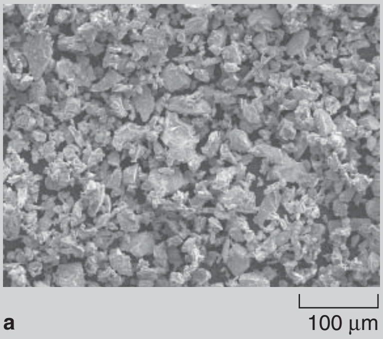


Figure 4. SEM images of 1100 Al-alloy; (a) virgin powder and (b) cryomilled powder after 8 hours.



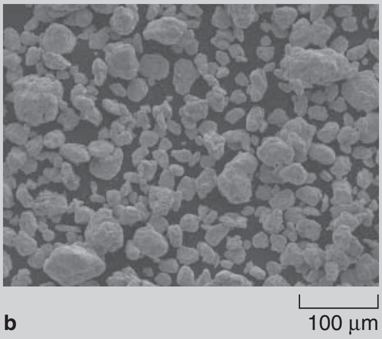


Figure 5. SEM images of CP titanium; (a) virgin powder and (b) cryomilled powder after 8 hours.

EXPERIMENTAL APPROACH

Series 1100 aluminum, commercially pure (CP) titanium, Ti-6Al-4V, and a blend of CP titanium with 6% aluminum and 4% vanadium (designated as CP Ti-6Al-4V) are cryogenically milled in a Union Process, Szegvari mill, Model No. S1, (Akron, Ohio) modified for liquid nitrogen and argon use. Stainless steel balls are used as milling media at a particular ball-to-charge ratio for a given material. A 30:1 ratio of ball diameter-to-charge size is common for milling metallic powders. The milling media and ball diameter are established by the powder to be milled. The representative variables that are established for a given cryomilling run are powder weight–1 kg, milling time–8 h or greater, ball-to-weight ratio–30:1 (varies with material), speed–180 rpm or greater.

After cryomilling, the light alloys are degassed to remove any control agents that have been added to prevent the powder from agglomerating above a selected particle size. Stearic acid is often used as the control agent in a concentration of less than a fraction of one percent. For titanium, degassing is typically conducted in a vacuum at 10^{-6} torr with a 3 h hold at 540°C. The complete degassing cycle takes approximately twenty-four hours, including a cooling period.

Hot Isostatic Pressing and Spark Plasma Sintering

Nano- and near-nano-grained materials produced using cryomilling are subsequently processed using hot isostatic pressing or spark plasma sintering to consolidate the powders into a bulk product. Hot isostatic pressing is the simultaneous application of temperature and isostatic pressure. It differs from hot pressing in that the pressure is applied uniformly in all three directions rather than uniaxially. This process also allows simultaneous densification and bonding of powders or porous bodies. The processing parameters for HIPing CP titanium are consolidation temperature–815°C, and consolidation pressure–69.0 MPa.

Spark plasma sintering is conducted at California Nanotechnologies using a Syntex Inc., Dr. Sinter Lab ™, model SPS-515S (Kanagawa, Japan). In SPS, powder is placed in a graphite die and loaded uniaxially while a pulsed electric current is applied through graphite punches (Figure A). The graphite die produces disks 20 mm in diameter by 6.6 mm in height. A type-K thermocouple is inserted into the die wall to monitor and control die temperature.

Sintering parameters in SPS are provided in Table A for the experiments used for virgin and cryomilled aluminum, CP titanium, Ti-6Al-4V, and CP Ti-6Al-4V.

Microstructural analysis was performed at California Nanotechnologies using a JEOL, Model No. JSM-7000F, Field Emission Scanning Electron Microscope (Tokyo, Japan). Microhardness was measured using a Struers hardness tester, model S140 (Copenhagen, Denmark). A 300-gram load was used for the aluminum samples, and a 1,000-gram load was used for the titanium samples. Rockwell hardness measurements were conducted using an Instron, model 2001R (Norwood, MA). Hardness measurements were carried out taking a minimum of five indentations on each specimen. Tensile strength and shear strength testing were conducted using an Instron, Satec System, Model No. 5590, (Grove City, PA). Shear strength testing was conducted using a single shear test fixture.

Figure A. Spark plasma sintering process.

Table A. Typical Spark Plasma Sintering Parameters

Element	Al (1100)	CP Ti	Ti-6Al-4V	CP Ti-6Al-4V
Temperature (°C)	515	850	850	850
Pressure (MPa)	47	60	60	60
Time at Temperature (min.)	5	4	4	4

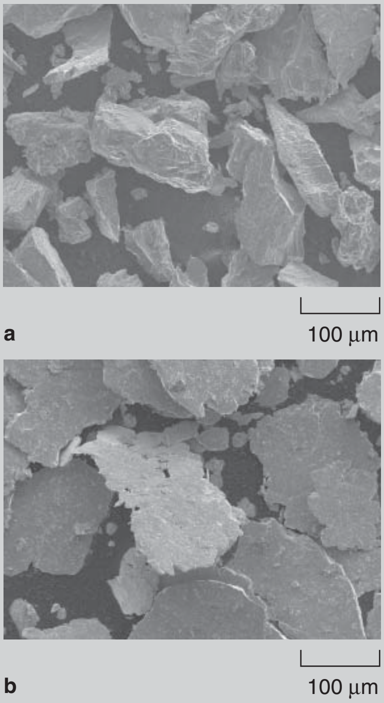


Figure 6. SEM images of Ti-6Al-4V; (a) virgin powder and (b) cryomilled powder after 5 hours.

to dislocation motion/generation in materials that exhibit plastic deformation

$$\sigma_o = \sigma_i + kd^{-1/2}$$
$$H_o = H_i + kd^{-1/2}$$

where σ_o is yield stress, σ_i is friction stress opposing dislocation motion, k is a constant, and d is the mean grain size.

Most of the mechanical property data on nanocrystalline materials have pertained to hardness, although some tensile test data has become available, with these recent efforts summarizing the material behaviors.[3–6] It is clear that as grain size is reduced through the nanoscale regime (<100 nm), hardness typically increases with decreasing grain size and can be several times (i.e., ~2–7) greater for pure nanocrystalline metallic materials (~10 nm grain size) than for large-grained (>1 µm) metallic materials.

When comparing the mechanical properties of the fine-grained, near-nano-, and nanocrystalline materials with the properties of conventional materials above, the increases shown by the cryomilled powder materials corroborate the Hall–Petch relationship, which predicts the strengthening of materials by reducing the average crystalline (grain) size.

CONCLUSION

The mechanical properties of cryomilled light alloys are greater than those of conventional materials. In cryomilling in nitrogen, aluminum was 3.0 times harder than that of the virgin (micron size) aluminum material, while the shear strength was 2.1 times greater than that of the virgin material. In cryomilling CP Ti in nitrogen, the average ultimate shear strength of cryomilled CP Ti material was 648.1 MPa. This is greater than the minimum ultimate tensile strength specified for conventional CP Ti, grade 4, material.

Cryomilling in argon also greatly improved the mechanical properties of the light alloys. In preliminary efforts, titanium alloys processed via cryomilling, plus high temperature vacuum degassing, and SPS-consolidation improved the mechanical properties. The Ti-6Al-4V alloy increased in hardness from 33.3 HRc in the virgin material, to 38.9 HRc in the cryomilled material. The tensile strength increased from 982.1 MPa in the virgin material to 1151.8 MPa in the cryomilled material. The CP Ti cryomilled with 6% aluminum and 4% vanadium elemental powders also showed an increase in strength from the values typically reported for CP Ti, achieving a hardness of 39.8 HRc and a tensile strength of 731.1 MPa. California Nanotechnologies is conducting ongoing efforts in parameter optimization (milling, degassing, blending, HIPing, and SPS-consolidating) and yielding further increases in mechanical properties—to be reported by second quarter 2011.

Figure 7. SEM of consolidated Ti-6Al-4V from as-received and spark plasma sintered powders.

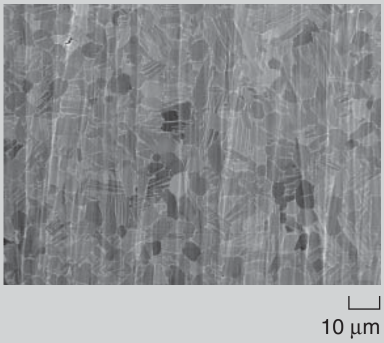


Figure 8. SEM of consolidated Ti-6Al-4V from cryomilled, degassed, and spark plasma consolidated powders.

Bulk powder consolidation techniques using hot isostatic processing and spark plasma sintering provide valuable processing techniques for consolidating fine-grained, near-nano-, and nanocrystalline powders produced using cryomilling processing. The properties of HIP and SPS-consolidated forms of fine-grained, near-nano-, and nano-crystalline powders are stronger and harder than consolidated forms consisting of conventionally-sized (micron-size) materials.

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Christopher Melnyk, vice-president, product development, David Grant is with California Nanotechnologies, Inc., Cerritos, CA 90703; Steven G. Keener, technical fellow, is with The Boeing Company, Huntington Beach, CA 92647; Steven Schroeder is a student at the University of Calgary, and Robert V. Gansert, president, is with Advanced Materials & Technology Services, Inc., Simi Valley, CA 93065. Mr. Melnyk can be reached at cmelnyk@calnanocorp.com.