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# Strategies for Improving Ductility of Cryomilled Nanostructured Titanium

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**Abstract.** The room temperature tensile behavior of commercially pure titanium (CP-Ti), cryomilled under different conditions and forged quasi-isostatically into bulk form, was studied in detail. The results demonstrate that the ductility of cryomilled titanium can be improved, and that the mechanical properties can be tailored using three specific strategies: the use of liquid argon as cryomilling media, introduction of coarse grained regions, and low temperature heat treatment. Cryomilling in a liquid argon environment, which differs from the widely used nitrogen cryogenic environment, was found to have a particularly strong influence on ductility, as it prevents nitrogen embrittlement. The contribution of coarse grains and heat treatment to ductility are also introduced and discussed using a comparative approach.

## Introduction

Coarse grained, commercially pure (CP) grades of Ti are known to exhibit elongation to failure values of up to 40-50% during room temperature tensile testing, depending on factors such as chemistry, processing route, texture and sample geometry [1]. As is the case for many metallic materials, however, it is a challenge to retain this ductility in nanostructured and ultrafine grained (UFG) CP-Ti [2-4]. In several previous studies on various metallic systems, this behavior has been attributed to a number of factors, including extrinsic processing artifacts such as porosity, insufficient bonding, and impurities [5], as well as to intrinsic microstructural factors related to deformation mechanisms, such as high density of lattice imperfections and small size grains resulting in a low strain hardening ability [6]. Whereas the elimination of processing artifacts is a required first step, modifications to the intrinsic microstructure of CP-Ti can be effectively implemented to modify mechanical behavior. As an example, according to Considére's criterion [7], a high strain-hardening rate is essential for good uniform elongation because it can help delay necking instabilities. If a material has a high strain hardening rate, an extension of a premature necking can be impeded by hardening of local necking part, so that the other gauge part can be elongated and hardened uniformly. [4, 8].

For many engineering and biomedical applications of CP-Ti, a high ductility is required, in addition to a high strength, to provide fracture toughness. More recent studies utilizing severe plastic deformation (SPD) techniques accomplished retention of some ductility while increasing the strength for bulk nanostructured CP-Ti [9-15]. For example, in related work, Sergueeva et al. [9] utilized equal channel angular pressing (ECAP) and high pressure torsion (HPT) methods to obtained bulk nanostructured CP-Ti samples which exhibit up to 790 MPa ultimate tensile strength (UTS) and 14% tensile elongation to failure. Recent published studies performed by Stolyarov et al. [15] and Zhao et al. [10] report promising results. In these studies, the retained high ductility is attributed to several different mechanisms derived from the presence of unique microstructural features, such as bimodal microstructures [16, 17], twin boundaries [18], high angle grain boundaries and reduced dislocation densities via annealing [19]. The micro grains that are present in

bimodal materials are known to suppress crack growth and facilitate strain hardening as a result of increased spacing for significant numbers of dislocations to intersect with each other and consequently accumulate during deformation [20]. Twin boundaries have large capacity for dislocation multiplication to give high strain hardening rate and large plastic strain. Reduced dislocation density regains strain hardening by increasing dislocation accumulation capacity [18].

The present investigation was motivated by the lack of promising results in the particular case of bulk nanostructured materials synthesized via powder metallurgical routes, which are of interest given their potential in commercial applications. Accordingly, cryomilling was utilized herein as the principal processing technique to produce nanostructured powders of CP-Ti. Cryomilling is essentially a mechanical ball milling technique which uses liquid nitrogen or liquid argon as the milling environment. High strain rates, large cumulative strains and a cryogenic temperature during processing enable the development of heavily deformed, nanocrystalline grains with large angles and deformed boundaries by limiting recovery while the contamination (generally O, N, Fe from milling environment) is lower due to limited diffusion [21, 22].

The experimental results obtained for cryomilled CP-Ti herein are discussed in the light of relevant published studies; those aimed improving the ductility of nanostructured CP-Ti and studied underlying scientific phenomena, in order to provide an overview of the various strategies. Accordingly, three specific strategies emerge: the use of liquid argon as cryomilling media, introduction of coarse grained regions, and low temperature heat treatment.

## Experimental Procedures

In this study, CP-Ti (Grade 2) powder (Advanced Specialty Metals, Nashua, NH) with an average particle size of 55 μm was used as the starting material. The as-received powder had a chemical composition of 0.190% wt. O, 0.0165% wt. N, 0.0030% wt. C and 0.013% wt. Fe. Cryomilling experiments were carried out in a stainless steel tank using a modified 1-S Szegvari-type attritor (Union Process, Inc., Akron, OH), stainless steel balls of 6.4 mm and a cryogenic medium for 8 hours. Either liquid argon (92 ± 5 K) or liquid nitrogen (82 ± 5 K) was continuously introduced in to the tank as the cryogenic medium by a temperature controller. Stearic acid ($CH_3(CH_2)_{16}COOH$) (0.4% wt. of Ti powders) was used during cryomilling in liquid argon as process control agent (PCA) to excessive cold welding of the powders. Cryomilling experiments involving liquid nitrogen did not require use of PCA as there was no excessive cold welding during the process. The cryomilled powders were always handled in an inert atmosphere using a closed powder transfer can and argon glove box. As it will be discussed in following sections, several different compositional mixtures of liquid nitrogen cryomilled, liquid argon cryomilled and as-received powders were prepared using a V-shape blender in order to study the effects of coarse grains in the microstructure. The compositional mixtures included in this study are listed as;

- 100% liquid nitrogen cryomilled
- 100% liquid argon cryomilled
- 50% liquid nitrogen cryomilled + 50% as-received
- 85% liquid argon cryomilled + 15% as-received
- 15% liquid argon cryomilled + 85% as-received

Cylindrical stainless steel cans 50.8 mm in diameter and 101.6 mm in height were filled with these powders. Prior to consolidation at 800˚C, hot vacuum degassing was carried using a tube furnace and a Turbo-V 70D Turbo molecular pump (Varian, Inc., Lexington, MA) at 810˚C temperature for 10 hours to pressures in the range of of ~$10^{-3}$ Pa.

The powders in the cans were consolidated into bulk materials using a two step quasi isostatic (QI) forging method at Advanced Materials and Processing Technologies, LLC (Riverbank, CA). In the first step, the cans were preheated to 800˚C and QI forged. In the second step, the cans were machined off and the remaining billet was reheated to 800˚C for second forging. Final billets of ~55

mm in diameter and ~40 mm height were obtained for producing specimens for tensile testing and microstructure analysis except for the 100% liquid cryomilled sample which fractured during second step of QI forging due to its brittle behavior. Flat dog-bone tensile specimens with gage dimensions of 10 mm length, 3.5 mm width and 2.5 mm thickness were prepared using a sample scaled according to standard ASTM B557-06 by Toyota Racing Development (Costa Mesa, CA). Heat treatments were done in air atmosphere using a conventional high temperature furnace.
The room temperature tensile behavior of the specimens was studied using an Instron (Norwood, MA) Model 8801 universal testing machine equipped with a video extensometer. Nominal strain rate during all tensile tests reported in this paper is $10^{-3}$ $s^{-1}$ controlled by crosshead displacement. The fracture surfaces of selected samples were observed using a FEI XL-30SFEG scanning electron microscope (SEM, FEI, Hillsboro, OR). The general microstructure of the powders and bulk samples were studied using a Philips CM12 transmission electron microscope (TEM) operated at 120 kV. Thin foils for TEM observation were prepared by mechanical grinding followed by ion milling using Gatan PIPS 691 system operating at 4kV. Chemical analysis of the obtained samples for N, O, C, Fe and H was performed in a commercial laboratory, Luvak, Inc. (Bolyston, MA).

## Results and Discussion

**Cryomilling.** Milling in a cryogenic environment alters the morphology and composition of the powders in several significant ways. These include: reduction of the grain size to the range of 20 nm, deformation of grain boundaries and formation of high angle grain boundaries, low-angle subgrain boundaries, increased dislocation density, and an increase in amount of impurities such as N, O, C, Fe and H. Details related to chemistry, morphology, microstructure and thermal stability of liquid argon and liquid nitrogen cryomilled CP-Ti powders were presented in a recent article by Ertorer et al. [11], and hence will not be reproduced here.

The cryomilling media selected (e.g., nitrogen versus argon), has a strong influence on chemistry. Accordingly, cryomilling introduces significant amounts of interstitial solute elements (i.e., O, N, C, H) and substitutional Fe [23], as a result of milling media and atmosphere. Especially, cryomilling in liquid nitrogen results in ~3% wt. nitrogen uptake which is known to be an interstitial solute element in hcp-Ti via occupying octahedral sites up to ~8% wt. [23]. The use of stearic acid ($CH_3(CH_2)_{16}COOH$) as PCA in liquid argon cryomilling experiments is required to avoid unacceptably low material yield, and it causes increased amount of C, H and O in powders [11]. However, a majority of these impurities are removed during the hot vacuum degassing step as the consolidated liquid argon cryomilled materials are found to have reduced C, H and O contents.

**Liquid argon vs. liquid nitrogen.** Table 1 summarizes and compares the amounts of O, N, C, Fe and H impurities measured for the bulk samples produced for liquid argon cryomilled and liquid nitrogen cryomilled powders. Analysis shows that the nitrogen content for the bulk materials produced from liquid nitrogen cryomilled powders is 2.890% wt. As mentioned in the previous section, the origin of this nitrogen can be attributed to the liquid nitrogen environment inside of the milling vessel. The higher amount of carbon in liquid argon cryomilled material is attributed to the residual carbon from stearic acid ($CH_3(CH_2)_{16}COOH$) after hot vacuum degassing. The origin of 0.620% wt. nitrogen content in 100% liquid argon cryomilled material is thought to be nitrogen in as-received powders, contamination from absorbed nitrogen in stainless steel cryomilling vessel and balls, and atmospheric contamination during $2^{nd}$ step of QI forging.

Results also reveal that, for liquid argon cryomilled powders, degassing step allowed removal of O and H originating from the addition of stearic acid during cryomilling.

| Samples | Oxygen (%wt) | Nitrogen (%wt) | Carbon (%wt) | Iron (%wt) | Hydrogen (%wt) |
|---|---|---|---|---|---|
| **100% liquid N cryomilled** | 0.620 | 2.890 | 0.044 | 0.120 | 0.0398 |
| **100% liquid Ar cryomilled** | 0.500 | 0.620 | 0.353 | 0.061 | 0.0213 |

Table 1. The amount of O, N, C, Fe and H elements in QI forged bulk samples of all liquid nitrogen cryomilled powders and all liquid argon cryomilled powders

Fig. 1 compares the room temperature tensile behavior of 100% liquid argon cryomilled, QI forged sample to that of 50% liquid nitrogen cryomilled + 50% as-received, QI forged sample. As shown in the figure, the 100% liquid argon cryomilled sample provided ~4% tensile elongation with ~1000 MPa UTS, while the 50% liquid nitrogen cryomilled + 50% as-received sample failed in the elastic region (e.g., without yielding). It is worth noting, however, that the can containing 100% liquid nitrogen cryomilled powders fractured prematurely during the second step of QI forging and no specimens could be obtained for tensile testing.

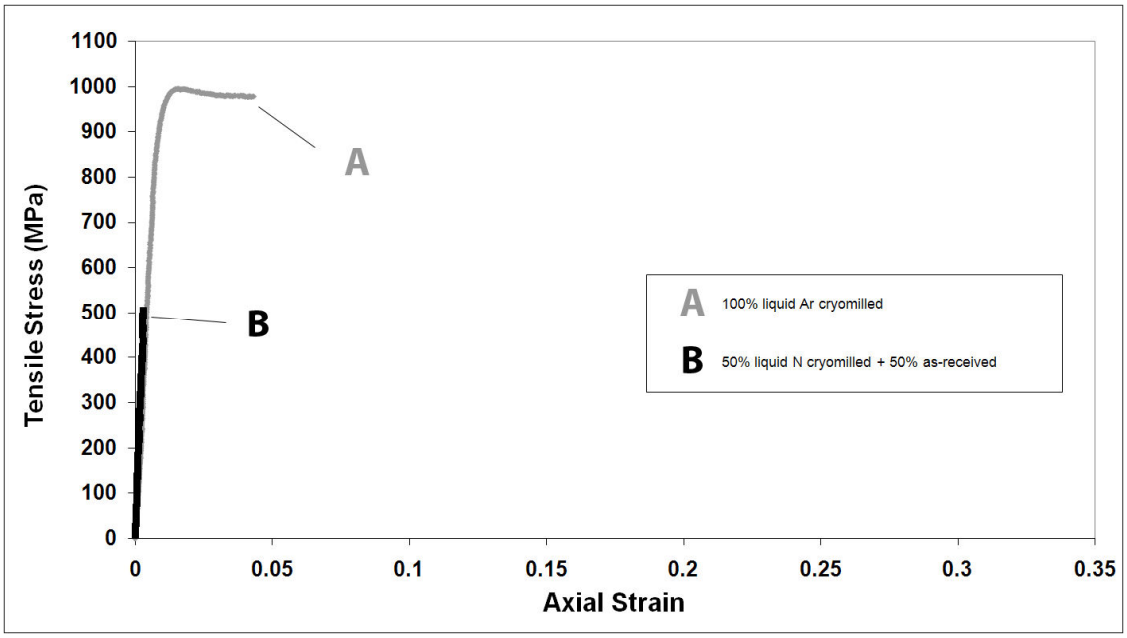


Figure1. Room temperature tensile test plots comparing liquid argon milled against liquid nitrogen cryomilled CP-Ti sample

The SEM micrographs from fracture surfaces of prematurely failed 100% liquid nitrogen cryomilled material and tensile tested 50% liquid nitrogen cryomilled + 50% as-received specimen are presented in Fig. 2. Both micrographs present similar features which are consistent with brittle fracture. Accordingly, trans-granular cleavage surfaces were predominant also with some features of intergranular fracture [24].

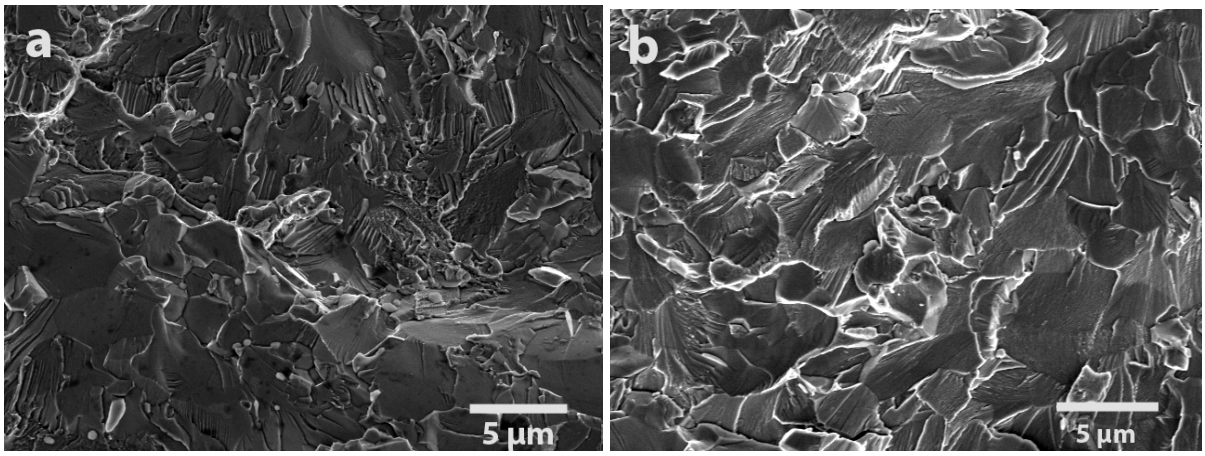


Figure 2. SEM micrographs from fracture surfaces of (a) failed 100% liquid nitrogen cryomilled sample during QI forging (b) tensile tested 50% liquid nitrogen cryomilled + 50% as received sample

Fig. 3 presents the SEM micrograph from the fracture surface of tensile tested 100% liquid argon cryomilled specimen. The deep dimples observed are evidence to plastic deformation and this is remarkably different than the ones presented in Fig. 2.

The brittle behavior of samples containing liquid nitrogen cryomilled powders is attributed to the high nitrogen content in the microstructure. The high nitrogen content has deleterious effect in terms of the ductility of Ti and this is widely documented in literature [11, 23, 25]. Detailed experimental studies and microstructural analysis are in progress related to the presence of nitrogen in cryomilled Ti and the associated deformation mechanisms.

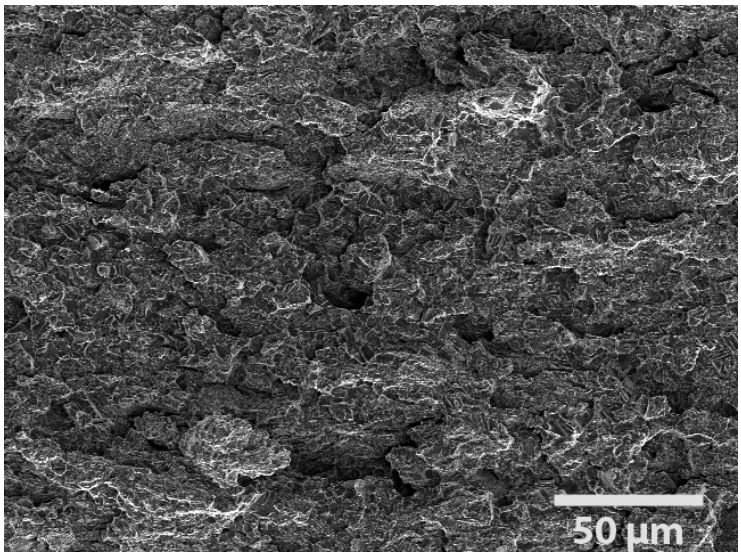


Figure 3. SEM micrograph from fracture surface of tensile tested 100% liquid argon cryomilled specimen

Accordingly, grain boundary and sub-grain boundary segregation of interstitial solute atoms (i.e., mainly nitrogen) is thought to be the dominant mechanism of embrittlement. Despite the high solid solubility limit of nitrogen in hcp-Ti lattice, linear and planar defects are favorable location for nitrogen atoms due to their high surface energies [6]. The non-equilibrium processing routes (i.e., cryomilling, QI forging) which are known to facilitate formation of high energy surfaces such as non-equilibrium grain boundaries, dislocation network and sub-grain structures, provide suitable sites for nitrogen segregation. The observed fracture surfaces for nitrogen cryomilled Ti samples supports this idea with the evidence of crack propagation through boundaries.

In the early study, Conrad [23] reports that interstitial solute atoms act as strong barriers for dislocation motion at low temperatures (i.e., cryomilling temperatures), which is thought to be applicable to cryomilled Ti in present study and may be effective in formation of nitrogen rich dislocation arrays. As discussed in same study, higher temperature treatments and processing (i.e., degassing and QI forging) removes the barrier effect caused by the solute atoms due to thermal activation. For cryomilled Ti, this is thought be effective in realignment of the dislocation arrays and thereby leading to the formation of a recrystallized structure with nitrogen rich grain boundaries. Sun et al. [26] previously studied the thermal stability of cryomilled Ti and relevant discussions were made in detail based on the different annealing response of liquid nitrogen cryomilled Ti (recrystallization was observed between 400-500 ˚C), compared to liquid argon cryomilled Ti. Also there is published evidence on grain boundary segregation for other cryomilled material metal systems [19, 27]. Recent work by Zhao et al. [28] indicates that the grain boundary segregation of nitrogen in nanostructured Ni prepared by cryomilling and QI forging caused an evident embrittlement.

Addition to embrittlement via initiating crack growth, grain boundary segregation will suppress grain boundary sliding [25, 29], which is widely known to be a dominant deformation mechanism in nanocrystalline and ultrafine grained materials [30, 31].

Independent from the grain boundary segregation, solute atoms at grain interiors also diminish plasticity as they limit the dislocation slip at room temperature and thereby reduce plastic deformation [32]. Therefore, higher total interstitial solute concentration in Ti will adversely influence ductility. The presence of the TiN phase may also effectively contribute to embrittlement as reported in an earlier study by Shen et al. [33] and efforts to locate and identify this phase are currently underway.

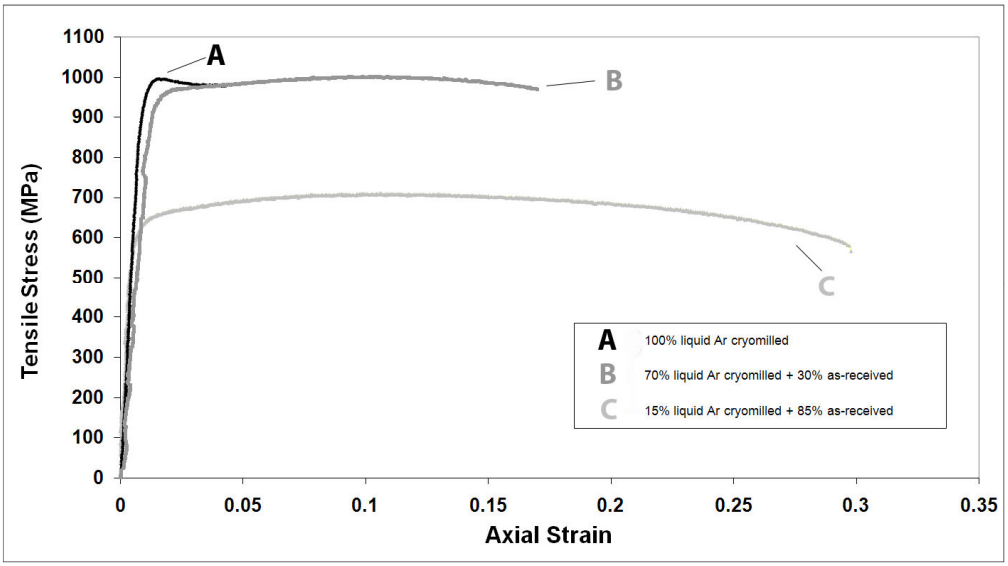


Figure 4. Room temperature tensile test plots comparing materials with different as-received powder content

**Addition of coarse grained powders.** Fig. 4 compares the room temperature tensile behavior of QI forged 100% liquid argon cryomilled material presented in the previous section, to those of QI forged liquid argon cryomilled + as-received powder blends. As can be seen from the curves, the tensile elongation of 70% liquid argon cryomilled + 30% as-received sample is approximately four times larger than tensile elongation of 100% liquid argon cryomilled sample with very small loss in yield strength. The tensile elongation of 15% liquid argon cryomilled + 85% as-received sample was largest as a result of highest as-received powder content. However, the strength is much lower due to highly reduced cryomilled powder content which provides strength.

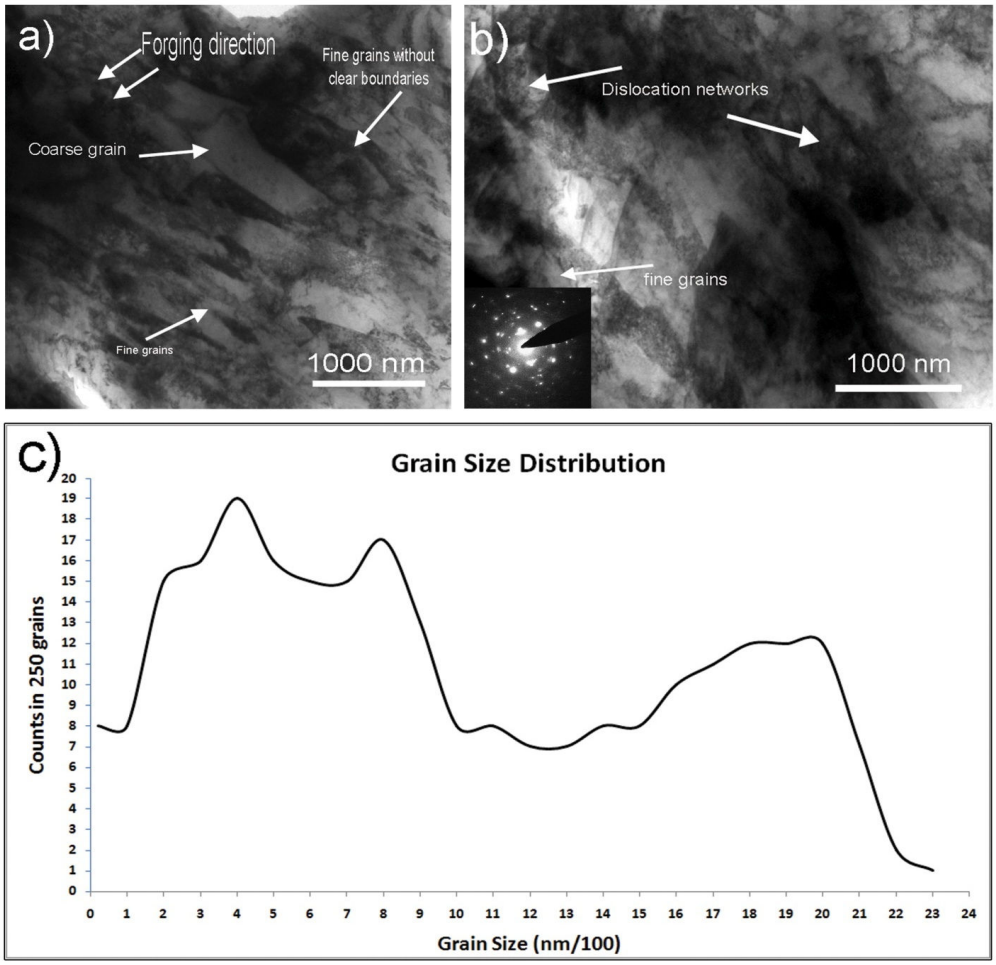


Figure 5. (a) and (b) are TEM micrographs (c) grain size distribution from multimodal 85% liquid argon cryomilled + 15% as received, QI forged sample [12]

Fig. 5 shows the TEM micrographs and grain size distribution for the 85% liquid argon cryomilled + 15% as-received material previously presented in the paper by Ertorer et al. [12]. The multimodal structure representing a wide grain size distribution range instead of a discrete bimodal distribution is thought result of two factors. First, the distribution of grains in the starting powder and second, grain growth during the degassing and QI forging steps. The deformation introduced during QI forging is also thought to effectively influence the final grain size and orientation as grains seem to be elongated perpendicular to the forging direction.

The results indicate that the ductility of QI forged samples increases with increasing as-received powder content. Similar studies previously done on cryomilled Al alloys by Tellkamp et al. [16], Han et al. [34], Witkin et al. [35], and a recent study cryomilled Ni by Zhao et al. [36] provided similar results while modeling studies by Ovidko et al. [20, 37] agree with these results. As discussed in the introduction part, the large grains can increase strain hardening ability by providing enough space for significant numbers of dislocations to intersect with each other and consequently accumulate during deformation, and therefore enhancing the uniform elongation and ductility. Moreover, the large grains are known to suppress crack growth and thereby enhance ductility.

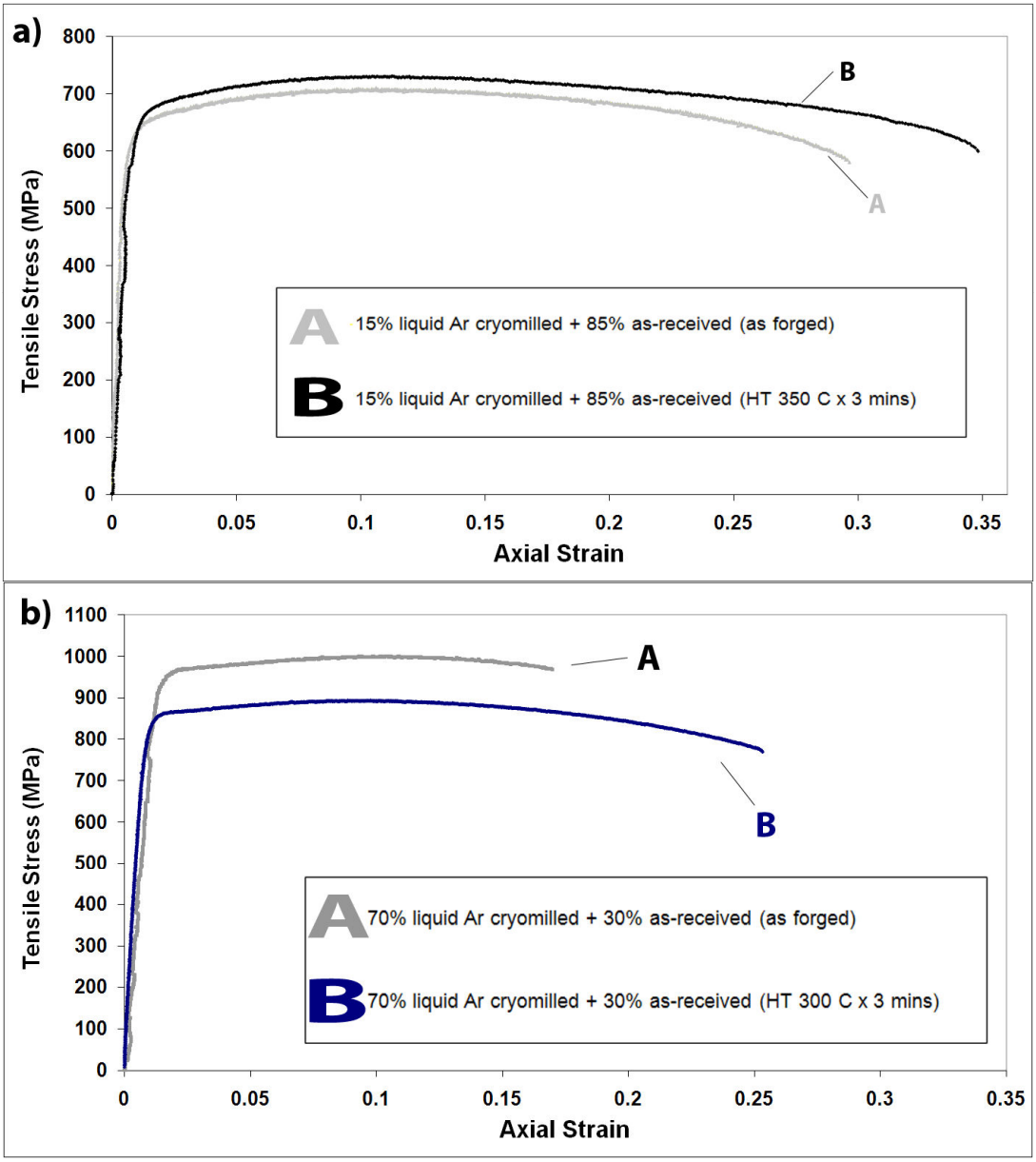


Figure 6. Room temperature tensile test plots for heat treated (a) 15% liquid argon cryomilled + 85% as-received, and (b) 70% liquid argon cryomilled + 30% as-received, QI forged CP-Ti

The retained high strength may be attributed to enhanced strain hardening as a result of larger effective area for dislocation pile-up and grain boundaries acting as dislocation sources [20, 35]. Further studies are in progress with the goal of optimizing the strength and ductility by adjusting the as-received powder content in the material. Powder metallurgical routes that are being followed are advantageous in these terms, as it is possible to adjust the volume fraction and distribution of coarse grains.

**Low temperature & short time heat treatments.** Fig. 6 shows that low temperature and short time heat treatments can be effective for improving ductility in nanostructured Ti. An increase in both strength and ductility has been observed for 15% liquid argon cryomilled + 85% as-received, QI forged Ti sample after 3 mins heat treatment at 350 ˚C. For the 70% liquid argon cryomilled + 30% as-received, QI forged Ti sample, after 3 mins heat treatment at 300 ˚C, increased ductility and reduced strength has been observed.

Despite some published studies, the microstructural mechanisms behind the significant effect of low temperature and short time annealing on these materials are currently elusive. Despite the

limited amount of experiments done and lack of detailed microstructure studies, these preliminary results suggest that low temperature and short time heat treatments can be effectively used to improve ductility and fracture toughness for cryomilled CP-Ti when performed using the correct parameters. In a related earlier study, Valiev et al. [13] on ultrafine grained CP-Ti also report on the dramatic effect of low temperature short time heat treatments. In this study, both the strength and ductility was enhanced after heat treatment at 300 ˚C for 10 mins for HPT CP-Ti. This effect was attributed to ordering of defect structures which is thought to lead the enhancement of grain boundary sliding as deformation mechanism. Moreover, annealing decreases dislocation density in the microstructure, and therefore increases strain hardening ability and ductility.

In the case of cryomilled Ti blended with coarse grained powders, multiple mechanisms may be responsible for the changes in mechanical behavior. Accordingly, recovery effects on low angle boundaries and reduction in dislocation density at grain interiors may be responsible from the observed ductility as is the case for conventional metals [38]. On the other hand, short time heat treatments in relatively low temperatures (i.e., below recrystallization temperatures) as implemented in the current study may facilitate generation of new dislocations sources from fine grain/coarse grain boundaries during straining. This effect might be responsible from the strengthening observed in 15% argon cryomilled + 85% as-received, QI forged Ti sample as the amount of coarse grains is much larger. Similar observations were presented in the comprehensive experimental study by Huang et al. [38].

## Conclusions

This study suggests three main processing strategies that are found to be very effective on tensile ductility and fracture toughness of cryomilled commercially pure titanium. Results are presented using comparative figures to reveal the significance of each strategy. Accordingly;

- Use of liquid argon instead of liquid nitrogen as cryomilling medium is the foremost strategy to produce materials useful for engineering applications. The brittle behavior of liquid nitrogen cryomilled material is attributed to the segregation of nitrogen atoms to high energy planar defects and thereby reducing the plasticity dramatically.
- Addition of coarse grained as-received powders are reported to be very effective for improving ductility of nanostructured Ti obtained via cryomilling. This is mainly attributed to the suppression of crack growth in coarse grains which is widely known in literature.
- The use of low temperature and short time heat treatments for modifying the microstructure are found to be useful for improving ductility. Despite the underlying mechanisms are not fully understood, dislocation re-alignment is thought to be the fundamental mechanism.

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