

Mechanochemical Processing of Nanocrystalline Ti-6Al-4V Alloy

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Abstract

Synthesis of nanocrystalline Ti-6Al-4V was explored using mechanochemical processing. The reaction mixture comprised of CaH_2 , Mg powder, anhydrous AlCl_3 , anhydrous VC1_3 and TiCl_4 . The milled powder (reaction product) primarily consisted of nanocrystalline alloy hydride having a composition $(\text{Ti-6Al-4V})\text{H}_{1.942}$, along with MgCl_2 and CaCl_2 as by-products. Aqueous solutions of nitric acid, sulfuric acid and 1% sodium sulfite were found to be very effective in leaching of the chlorides from the milled powder. The $(\text{Ti-6Al-4V})\text{H}_{1.942}$ on dehydrogenation at 375°C resulted in nanocrystalline Ti-6Al-4V alloy powder.

I INTRODUCTION

Mechanochemical processing is a novel and cost effective method of producing a wide range of nanopowders. It involves the use of conventional high energy ball mill to initiate chemical reactions and structural changes¹. Production of nanoparticles using mechanochemical processing requires use of suitable precursors². Very often, reagents such as oxides, carbonates, sulfates, chlorides, fluorides, hydroxides etc. are used as the precursor material. The milling action influences the reaction kinetics in a reacting powder mixture as a result of the intimate mixing and refinement of the grain structure to the nanometer scale, allowing the reaction to occur during the actual milling. Chemical reactions, which normally require high temperatures, can thus be activated during room

temperature milling. The resulting product is formed as individual nanometer sized grains in a by-product matrix in relatively short time. The nanopowder is then recovered by leaching the by-product using suitable solvents³⁻⁵. Milling is occasionally followed by a low temperature heat treatment to ensure the reaction is complete before the by-product is removed, leaving the pure, non-agglomerated nanopowder. Figure 1 illustrates how the mechanochemical process can circumvent the multistage process normally used to produce titanium⁶.

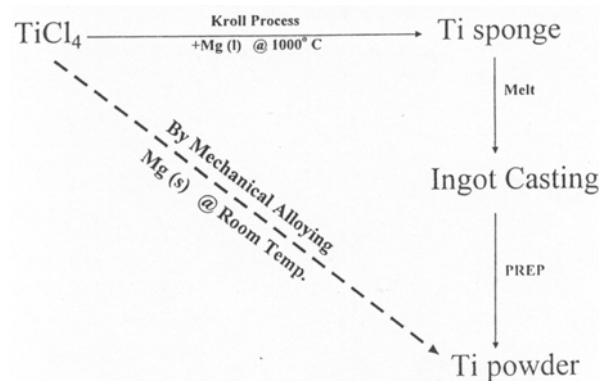


Fig. 1 - Mechanochemical synthesis of titanium powder[6].

Mechano-chemical Processing of Titanium Based Materials

McCormick et al. were the first to successfully demonstrate the use of mechanochemical processing (MCP) to synthesize titanium from TiCl_4 with magnesium as a reducing agent⁷. Using magnesium as a reducing agent, the milling had to be carried out for extended period of time for the process to reach completion. According to a recent study, premilling of magnesium is known to expedite the MCP of titanium, a more drastic reduction in milling time is achieved by replacing magnesium with CaH_2 ⁸. The study also suggest that use of CaH_2 in combination with magnesium makes the MCP of titanium less explosive and more controllable. CaH_2/Mg has been successfully used as reducing

agent to synthesize titanium based advanced lightweight materials such as Ti-Al by co-reduction of chlorides of constituent components⁹⁻¹⁰. This paper is an overview of our recent work on mechanochemical processing of nanocrystalline Ti-6Al-4V alloy.

II EXPERIMENTAL PROCEDURE

CaH₂, Mg powder, anhydrous AlCl₃, anhydrous VC1₃ and TiCl₄ were used as the starting materials. NaCl was used as a reaction diluent. The charge comprising of 10 gm of reactant mixtures was milled using a Spex 8000 ball mill, consisting of hardened steel vial and 3/8th inch steel balls as the grinding media. The proportion of the reactants in the reactant mixture was in accordance with the chemical equation represented by equation 1. Milling was carried out, under an argon atmosphere to minimize atmospheric contamination. The effect of ball-to-charge ratio was studied by varying the ball-to-charge ratio from 8:1 to 15:1. A thermocouple was attached to the outside surface of the vial to determine the temperature change of the vial during milling. Upon completion of the milling process, powders were unloaded from the vial in an argon atmosphere. The milled products were leached to remove the by-products. The slurry obtained after leaching the by-product was centrifuged to recover the milled product ((Ti-6Al-4V)H_x). The effect of post-reaction milling was studied by carrying out the post reaction milling for different interval of time. The dehydrogenation behavior of milled product, (Ti-6Al-4V)H_x was studied using a Perkin-Elmer DTA 7 Series Thermal Analyzer. The surface area of the powder samples was determined using a Quantasorb QS-11, BET apparatus. The metal hydride (Ti-6Al-4V)H_x powder samples were consolidated using hot isostatic pressing (HIP'ing). HIP'd Ti-6Al-4V samples were annealed at 1000°C for 1 hour in vacuum.

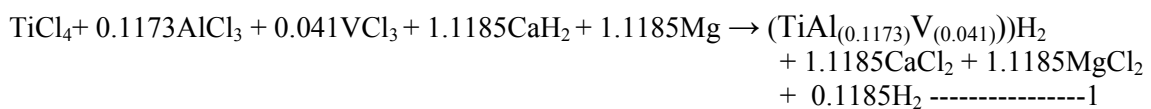
Structural transformation was monitored using the Philips x-ray diffractometer (XRD) with Cu K α radiation. Hitachi S-2300 scanning electron microscope was used to study the microstructure and grain size of the consolidated samples. Thin foils for transmission electron microscopy (TEM) analysis were prepared by conventional electro-thinning technique. The consolidated sample was also studied using a JEOL JEM 2010 TEM operating at 200kV.

Neutron activation analysis and inductively coupled spectroscopy were used to determine the concentration of impurities in the final product. For neutron activation analysis samples were irradiated for 2 minutes with a thermal neutron flux of the order of 10¹² ncm⁻² s⁻¹. A cooling time of 10 minutes and counting time of 200 seconds was used during this analysis. The counting system comprises of multichannel analyzer (MCA), coupled with the Ge (Li) coaxial 30-cm³ detector.

III RESULTS AND DISCUSSION

Synthesis of (Ti-6Al-4V) by MCP

Ti-6Al-4V alloy can be chemically represented as TiAl_(0.1173)V_(0.041). The probable reaction leading to the formation of Ti-6Al-4V alloy (TiAl_(0.1173)V_(0.041)) during the MCP can be represented by the following chemical equation.



The as-milled powder mixture contains Ti-6Al-4V in the form of hydride ((TiAl_(0.1173)V_(0.041)))H₂). As per the reaction represented by chemical equation 1 the as-milled powder mixture is also expected to contain CaCl₂ and MgCl₂ as reaction by-product.

The heat changes associated with the chemical reaction accompanying the MCP are likely to affect the temperature of the vial holding the powder mixture during the milling. Thus by measuring the vial temperature it is possible to monitor the progress of the reaction that accompanies the MCP. Figure 2 shows the temperature profiles of the vial. The curve A in Figure 2 represents the overall temperature profile due to the collision of the balls and the reaction that accompanies MCP. Curve B in Figure 2 represents the temperature profile due to chemical reaction alone. Curve B was obtained by subtracting the temperature rise due to the collision of the steel balls from the overall temperature profile (curve A) of the vial. The temperature rise in the vial due to the collision of the steel balls was determined by running the spex mill with stainless steel balls alone and measuring the vial temperature. From curve B, representing the heat changes in the vial due to chemical reaction alone it is evident that there is abrupt increase in the vial temperature in the initial stages of the MCP. Curve B also suggest that the chemical reaction accompanying the MCP is exothermic in nature and takes about 20 minutes for completion. The abrupt rise in vial temperature during the initial stages of milling is when the bulk of the powder mixture ignites. In the present case the time required to ignite the bulk of the powder mixture (t_{ig} , ignition time) is few minutes.

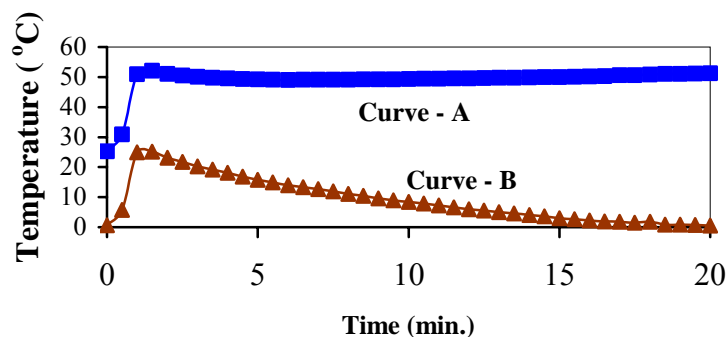


Fig. 2 - Temperature profiles of the vial.

Leaching of the Milled Powder Mixture

As mentioned earlier the milled powder mixture is accompanied with reaction by-product such as CaCl_2 and MgCl_2 . Therefore to separate the Ti-6Al-4V (hydride) from the milled powder mixture it is necessary to leach out these chlorides and unreacted reagents using a suitable leaching process. Due to the alkaline nature of the accompanying by-products (CaCl_2 and MgCl_2), the pH of the slurry, obtained by adding reaction product to water, is in the alkaline range (>7). Removal of chloride therefore should affect the pH of the slurry containing the milled powder. Figure 3 shows the variation in pH of the slurry at the different stages of the leaching process. In the initial leaching of the reaction product was attempted with a 5% formic acid solution. This led to an overall reduction in the chloride concentration to 1200 ppm. This was followed by washing of the reaction product with distilled water followed by final washing with ethyl alcohol.

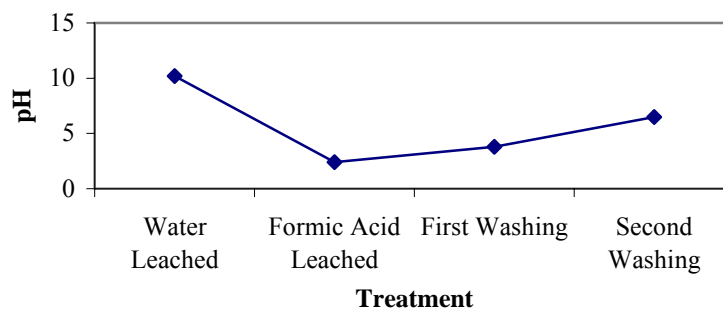


Fig. 3 - pH of the slurry at the different stage of the leaching process.

Leaching of the chlorides from the milled powder mixture was also attempted using several other methods involving use of boiling water, nitric acid, sulfuric acid and aqueous solution of sodium sulfite. The contaminants in the leached powder mixture were analyzed using neutron activation analysis. Inductively coupled spectroscopy was used to achieve extra level of accuracy in estimating contaminants in the leached powder. Figure 4 shows the effectiveness of a) hot water, b) sulfuric acid, c) nitric acid and d) sodium sulfite on the removal of chloride impurities from the milled powder mixture. Leaching with boiling water was found to be least efficient method of eliminating chlorides from the milled powder mixture., figure 4a. Even after leaching with boiling water for 40 minutes the chloride content in the milled powder mixture could not be reduced below 5000 ppm. Sulfuric acid, nitric acid and aqueous solution of sodium sulfite are more effective in leaching the chlorides (Figure 4b, Figure 4c and Figure 4d).

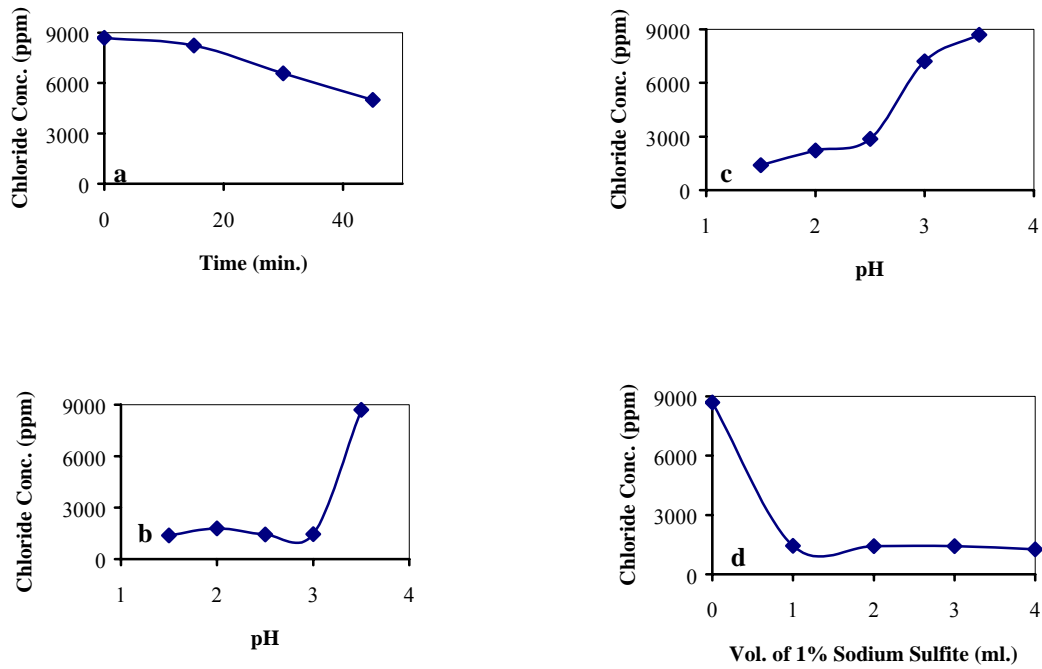


Fig. 4 - Effectiveness of a) hot water, b) sulfuric acid, c) nitric acid and d) sodium sulfite on the removal of chloride impurities from the milled powder mixture.

Effect of Milling Parameters on the Reaction Product

Figure 5 shows the effect of ball to powder ratio on the surface area of the final product. Beyond the ball to powder ratio of 10, the surface area of the reaction product increases linearly with the ball-to-charge ratio.

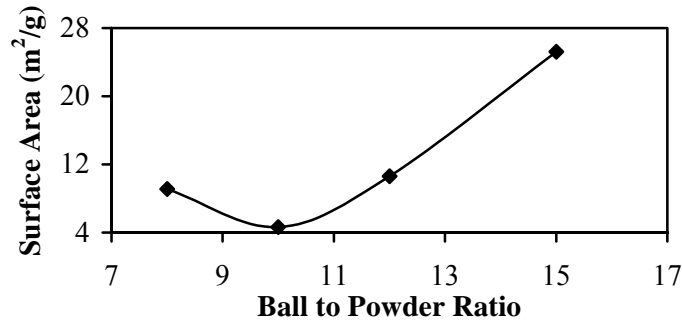


Fig. 5 -Effect of ball to powder ratio on the surface area of the reaction product.

Pre-milling of the reducing agents (CaH₂/Mg) used during the MCP of Ti-6Al-4V are likely to ensure homogenous mixing, prevent formation of “hot spots” and explosion during the milling process. Figure 6 shows the effect of pre-milling of CaH₂/Mg on the surface area of the leached milled powder (hydride form of Ti-4Al-4V). Pre-milling of CaH₂/Mg for five minutes results in the fine reaction product.

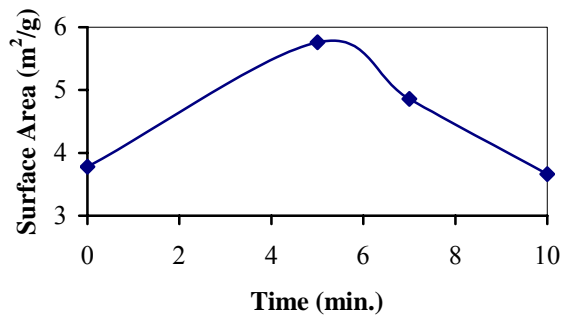


Fig. 6 - Effect of pre-milling time on the surface area of the reaction product.

As mentioned earlier, during the MCP of the Ti-6Al-4V it takes couple of minutes of milling time for the bulk of the powder mixture to ignite. And Ti-6Al-4V is formed as a hydride. Hydrides being brittle in nature, milling for extended period of time(post-milling) beyond ignition time t_{ig} should have an positive effect on the surface area of the

milled powder (reaction product). Figure 7 shows the effect of post-milling (milling beyond ignition time, t_{ig}) on the surface area of the milled powder. After 30 minutes of post-milling, the surface area of the milled powder begins to decrease possibly because of tendency of the fine powder to agglomerate, Figure 7.

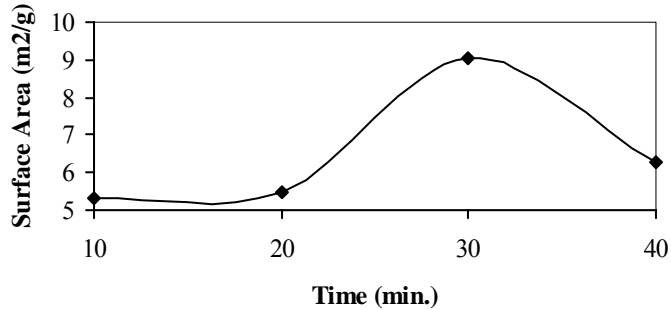


Fig. 7 - Effect of post-milling on the surface area of the reaction product.

Due to the highly explosive nature of the MCP of Ti-6Al-4V, it is essential to dilute the reactants with a chemically inert compound. Use of diluents decrease the overall heat evolution and lower the rate of combustion during the MCP. In the present study involving the MCP of Ti-6Al-4V, NaCl was used as a diluent. To study the effect of diluent on the milling process, concentration of NaCl in the reaction mixture was varied from 20 to 80 %. Figure 8 shows the effect of NaCl on the temperature profile of the vial during the milling process. From Figure 8 it is evident that the time required for the bulk of powder mixture to ignite (ignition time) during the milling process increases with the amount of NaCl.

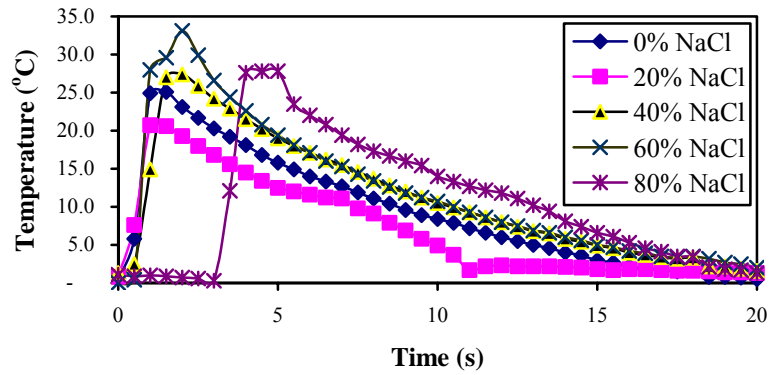


Fig. 8 - Effect of NaCl dilution on the temperature profiles of the vial

After thorough leaching the milled powder was examined using X-ray Diffraction (XRD), Figure 9. From the XRD pattern it appears that the leached product is primarily $(\text{Ti-6Al-4V})\text{H}_{1.942}$. The lattice parameter calculated for the cubic structure of $(\text{Ti-6Al-4V})\text{H}_{1.942}$ was found to be $a_{(\text{Ti-6Al-4V})\text{H}_{1.942}} = 4.4045 \text{ \AA}$. There were no peaks corresponding to the TiCl_4 , AlCl_3 , CaH_2 or Mg in the XRD pattern of the sample.

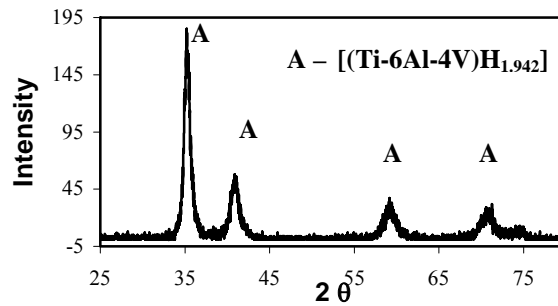


Fig. 9 - X-ray diffraction pattern of the leached reaction product.

The transmission electron photomicrograph, Figure 10, shows that the milled powder consists of particles which are agglomerates of nanosized particles. The SADP of the $(\text{Ti-6Al-4V})\text{H}_{1.942}$ suggest that the milled powder is nanocrystalline in nature, Figure 10.

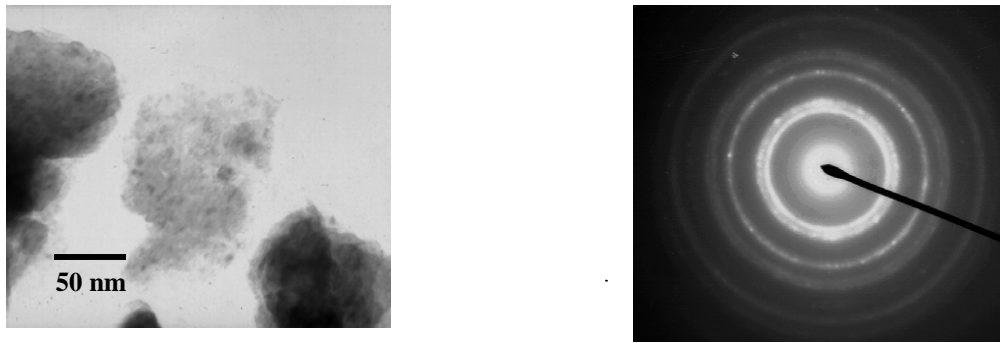


Fig. 10 - TEM bright field image and SADP of the milled powder

Dehydrogenation of the Reaction Product

Based on the differential thermal analysis results 375°C was chosen as the dehydrogenation temperature for the milled powder[(Ti-6Al-4V)H_{1.942}]. The (Ti-6Al-4V)H_{1.942} on dehydrogenation at 375°C results in nanocrystalline Ti-6Al-4V alloy powder, Figure 11.

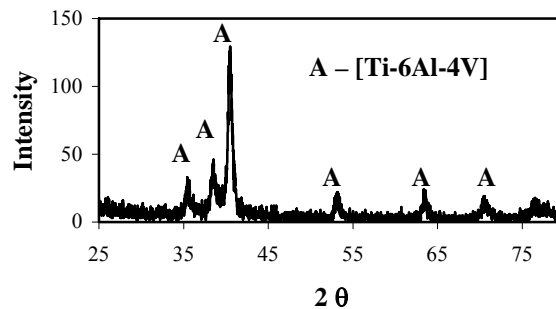


Fig. 11 - X-ray diffraction pattern of the leached reaction product after dehydrogenation.

Consolidation of the De Hydrogenated Reaction Product

Scanning electron microscopy of the HIP'd sample showed 5 % porosity, Figure 12. The presence of porosity in the consolidated Ti-6Al-4V samples could be due to the presence

of remnant salt during the leaching of the milled powder and/or due to the incomplete dehydrogenation of the leached reaction product.

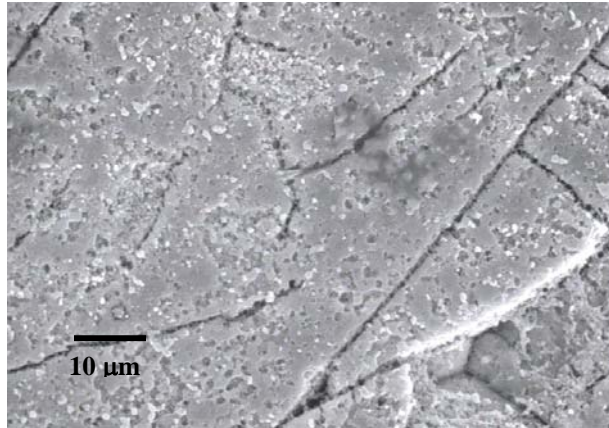


Fig. 12 - Scanning electron micrograph of the HIP'd sample

The as-HIP'd samples (with a grain size of 50-200 nm) showed microhardness of 1256 VHN.

IV CONCLUSIONS

The following conclusions can be drawn from the present investigation involving mechanochemical processing of nanocrystalline Ti-6Al-4V alloy:

- 1- The feasibility of mechanochemical alloying as a method for the combustion synthesis of $(\text{Ti-6Al-4V})\text{H}_{1.942}$ powder by co-reduction of metal chlorides of Ti, Al and V by CaH_2 and Mg has been established. The process occurs by initiation of the reduction reaction by mechanical milling. The reaction milling produces a nanocrystalline alloy hydride having a composition $(\text{Ti-6Al-4V})\text{H}_{1.942}$, with MgCl_2 and CaCl_2 as byproducts.
- 2- Aqueous solutions of nitric acid, sulfuric acid and 1% sodium sulfite were found to be very effective in leaching of the chlorides from the milled powder.

Parameters that controlled the kinetics of the reduction reaction include (i) pre-milling time (ii) ball-to-charge ratio, and (iii) NaCl dilution.

- 3- The (Ti-6Al-4V)H_{1.924} on dehydrogenation at 375°C results in nanocrystalline Ti-6Al-4V alloy powder.

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