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4 **The relationship between the green density and as-sintered density of nano-**
5 **tungsten compacts**
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18 **Abstract**
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21 Tungsten is a primary candidate material for certain structural applications in future
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23 fusion reactors. However, drawbacks associated with these applications include the need
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25 for a low ductile to brittle transition temperatures (DBTT) and significant demands for
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27 fracture toughness. A possible solution to these problems is nanostructuring of tungsten
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29 (nano-W; grain size < 100 nm) following the conventional and press-sinter route, which
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31 is quite economic. High green density and low temperature sintering are the critical
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33 factors for preserving nanoscale grains. Previous works, and our experience, have shown
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35 that it is nearly impossible to get high green density (> 40% relative density) of compacts
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37 for nano tungsten powders made by high-energy milling. This makes the material prone
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39 to rapid grain growth; with grain size well over 100 nm before complete densification,
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41 even at 1000°C. In this work, a high density green compaction method for nano-W
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43 powders was demonstrated, which can improve green density by at least 18% in relative
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45 density. Additionally, the effect of green density on the sintering behavior of nano-W was
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47 investigated.
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55 **Keywords:** Nano tungsten (Nano-W); High green density compaction; DBTT; grain
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1. Introduction

Tungsten has an excellent combination of high temperature properties (strength and thermal shock resistance), low-activation, low sputter yield, low tritium retention and good irradiation resistance [1-2]. This makes it a primary candidate material for certain structural applications in future fusion reactors, but brittleness problems remain an issue of concern. Materials for these applications need to have a sufficiently low ductile-to-brittle transition temperature (DBTT) and sufficiently high fracture toughness at elevated temperature. Within the lower temperature range of operating conditions, current tungsten materials are extremely brittle, which is detrimental for structural applications. Extensive research efforts have been directed towards lowering the DBTT of tungsten [1-2].

During recent years, nanostructuring of tungsten (nano-W, grain size < 100 nm) has received significant attention due to its potential for making more ductile tungsten based materials [2]. The high volume of grain boundaries of nano-W provides the possibility of shifting toward more readily operable deformation mechanisms in tungsten, such as from screw dislocation dominated (intra-granular dislocation activity) in coarse grains to edge dislocation or boundary dominated (grain boundary rotation and sliding) in nanoscale grains [3-4].

To achieve small grain sizes of tungsten, there are various bulk-processing methods available, mostly classified into two distinct approaches: top-down and bottom-up [5]. The first is top-down via severe plastic deformation (SPD) to reduce the grain size of a monolithic component, such as equal-channel angular processing (ECAP), high pressure

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4 torsion (HPT) and hot rolling. Wei and Kurishita et al. reported that when compared to
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6 coarse-grained counterparts, ultrafine grained tungsten demonstrated better high
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8 temperature properties, as well as improved ductility and toughness at lower temperatures
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10 [6-7]. The top-down approach is difficult to scale up and especially not suitable for near
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12 net shape fabrication of components. The second approach, bottom-up, involves
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14 densifying powders starting with a nano-scale size, and may involve developing novel
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16 methods for synthesis of nano W powders, and alternative consolidation techniques.
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18 Additions of grain growth inhibitors are advantageous, as well as high pressure-assisted
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20 sintering with short thermal exposure, both of which could assist in simultaneously
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22 obtaining high density and fine grain size [8-12]. For example, Wahlberg et al. reported a
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24 synthesis method which could control particle growth to produce uniformly yttrium
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26 doped nano-sized tungsten powders [10]. Zhou et al. have developed ultrafine grained
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28 tungsten using resistance sintering under ultra-high pressure (RSUHP) [12]. However,
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30 these processing techniques can only produce a minimum grain size in the range of 150-
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32 200 nm. Thus, processing strategies need to be further developed in order to obtain grain
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34 sizes less than 100 nm.
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45 Currently, the most promising method to make nano-W is still following the
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47 conventional press-sinter route. Compared with the alternative pressure-assisted rapid
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49 consolidation techniques, the press-sinter route has advantages in removing impurities
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51 and economic benefits [13]. Prior models and experiments showed that a potential press-
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53 sinter route, utilizing ultrahigh compaction pressure and low sintering temperatures,
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55 could preserve nanosized grains [13-15]. Johnson predicted that a starting W particle size
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57 of 40 nm, an ultrahigh compaction pressure of 2560 MPa and a sintering temperature of
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4 900°C can produce near fully dense W with a grain size below 200 nm [15]. The
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6 ultrahigh compaction pressure, i.e. high green density, would be the most critical factor
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8 for the successful press-sinter of nano-W.
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12 Previous works, and our own experience, have shown that it is nearly impossible to
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14 obtain high green density of compacts at room temperature for nano tungsten powders
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16 made by high energy milling [14-18]. Using common uniaxial or isostatic pressing, with
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18 pressures up to 1 GPa, it is very difficult to press nano-W powders to high green density,
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20 more than 40% of theoretical density, due to the large amount of surface area, strength
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22 and brittleness. A high volume percent of polymer binders can be used to increase the
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24 green density to a limited degree, but due to contamination issues this approach has
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26 limitations [13]. The low green density compacts require sintering at high temperatures
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28 and long times to achieve full densification. Unfortunately, the onset temperature for W
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30 grain growth during sintering nano W powders is in a very low temperature range, 800-
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32 900°C [14, 16]. At 1000 °C, W grains with a starting size of ~20 nm can grow to a size of
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34 about 300 nm in 1 hour, but with a relative density less than 90%. Early stage grain
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36 growth that exceeds the nanoscale is responsible for the coarsening of grains and occurs
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38 before any significant densification during heating to normal sintering temperatures [18].
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40 In order to achieve fully dense nano-W, a green compaction method that significantly
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42 improves the green density of nano-W powders is required.
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53 In this work, a novel method to produce green compacts of nano W powders has
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55 been recently developed that limits W grain growth during sintering. The high density
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57 green compaction is formed at a moderate temperature that is above its DBTT, but below
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4 temperatures that would cause rapid grain growth. This process can produce green
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6 compacts with high relative densities, which enable sintering at lower temperature for
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8 shorter times, minimizing grain growth. The effectiveness of improving the green density
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10 of the nano tungsten powder compacts through this process is demonstrated. A
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12 comparative dilatometer analysis of the sintering behaviors of nano tungsten compacts
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14 with 3 relative densities is presented.
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20 **2. Experimental**

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23 Nano W powder was prepared by using a unique high energy planetary ball milling
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25 (HEPM) process [18]. The combined revolution and rotation of the mill canister can
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27 generate an acceleration field that is nearly 60 times the force of gravity, which makes it
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29 highly efficient for the production of nano powders. The powder was milled for 6 hours
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31 in a mixture of heptane and ethanol. After milling, the powder was dried at room
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33 temperature under vacuum.
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40 Figure 1 schematically shows the high density green compaction process. The
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42 compaction was performed using a uniaxial press. Powders were pressed into a
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44 cylindrical shape with a diameter of 12.7 mm and weight of ~ 3 g. During compaction,
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46 the powder was heated to a given temperature under flowing argon at 0.2 L/min with a
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48 holding time at applied pressures of 10 min. Current steel die components can operate at
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50 temperatures up to 500°C. The high density green compaction of the nano-W powders
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52 were conducted at ambient temperature and at temperatures ranging from 200°C to
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54 500°C and under pressure of 200-800 MPa .
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After the compaction, samples with different relative green densities were sintered to study the effect of green density on the sintering behavior of the nano W powder. Previous results have shown that the HEPM process significantly enhances the sinterability of the nano tungsten powders, achieving near-full density at much lower temperatures, such as 1100°C for 1 hour. Sintering experiments were carried out in a dilatometer with flowing hydrogen and a heating rate of 10 °C/min, then held at 1100°C for 1 hour.

The nano W powder was characterized by using scanning electron microscopy (SEM) and X-ray diffraction. Green densities were calculated using geometrical dimensions. After sintering, densities of the samples were measured by using Archimedes method. Microstructural changes of the sintered samples were observed using SEM, and tungsten grain sizes were determined from SEM micrographs using the linear intercept method. To this end, five SEM micrographs were randomly taken on each specimen. Randomly positioned lines were drawn on the micrographs, and at least 100 intercepts were measured on each micrograph. The average grain size and standard deviation were then calculated.

3. Results and Discussion

Characterizations of nano W powder

Figure 2 shows the typical morphology of the nano W powder milled using the unique HEPM process. The milled powder has very fine particle sizes, less than 50 nm, but with agglomeration sizes to ~50-500 nm. The average W crystallite size was determined to be 12 nm by using X-ray diffraction (XRD) and the Stokes and Wilson

formula for grain size determination by peak broadening. The very small particles and the agglomerates make it difficult to press the nano-W powders to high green density.

High green density compaction

The high green density compaction was then used to press the nano-W powder. The purpose of this compaction process is to increase green density as much as possible prior to any early stage of grain growth during heating to sintering temperatures. Using the conventional uniaxial cold pressing method, the nano-W powders can only be pressed to ~40% relative density, which results in rapid grain growth prior to any significant densification. The effective temperatures should be higher than the DBTT of W particles such that the particles/agglomerates will plastically deform during compaction, thus achieving higher density, but lower than the temperature that would cause rapid grain growth.

Figure 3 demonstrates that green compaction at 450°C can markedly improve the green density compared to uniaxial pressing at ambient temperatures. As expected, at room temperature, with increasing pressure the relative density appears to approach an asymptotic value. Above 400 MPa, the relative density varies slightly, but the maximum relative density for the nano W powder pressed at room temperature was approximately 40%. In contrast, when pressing at 450°C, a continuous increase in green density was observed with increasing pressure. A significant increase of 18% in relative density (nearly a 50% improvement) was achieved at 800 MPa over the value achieved at the same pressure at room temperature.

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4 In general, a uniaxial compaction process can be described as having 3 stages:
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6 rearrangement, plastic deformation, and mechanical interlocking of powder particles. In
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8 the first stage of compaction, particle rearrangement occurs to fill the large gaps between
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10 particles. Then, in the second stage, plastic deformation of particles occurs as the main
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12 mechanism for further increasing the green density. For the nano-W powder, only ~40%
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14 green density was reached at room temperature, mostly attributable to rearrangement of
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16 particles and agglomerates. With increasing temperature of compaction up to 450°C, the
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18 plastic deformation played a more prominent role. It should be noted that there are two
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20 different regions of compaction seen for both temperatures. Above a critical pressure, the
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22 slope leveled off and there was only minor additional densification. Below the critical
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24 pressure, the compact proceeded via rearrangement and/or plastic deformation. At room
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26 temperature, the slope of the first region is nearly linear, indicating there was no plastic
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28 deformation. At 450°C, however, there was a significant increase of the slope between
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30 400 MPa and 600MPa, Figure 3, indicating the contributions of plastic deformation to the
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32 densification process.
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41 These results also indicate that the DBTT for the milled nano-W powder may be
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43 below 450°C, where powder plastic deformation contributes to the increase in green
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45 density. Other physical explanations of the data may also be possible, but definitively, the
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47 green compact density was dramatically improved.
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51 The effects of both the pressing temperature and the applied pressure on the relative
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53 density of green compacts of the nano-W powders are further shown in Figure 4.
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55 Generally, with higher temperature and higher pressure, green density is improved. It
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57 should be noted that under constant pressure, there is a transition temperature within the
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range of 200-300°C, where there is significant improvement in the compressibility of the nano-W powder. Previous investigations have shown that the DBTT of sintered W is ~ 400°C [19-20]. The high energy ball milled powder goes through severe plastic deformation during milling and, in this case the DBTT may shift from approximately 400°C down to much lower temperatures. Here, the transition within 200-300°C is indicative of the DBTT of the nano-W powder green compacts.

Effect of green density on grain growth

The densification and grain growth behaviors of the green compacts of nano W powders with different compact densities (~ 35%, 45%, and 55%) during sintering are shown in Figs. 5. With increasing green density, the linear shrinkage decreased not only during the heating process, but also during the isothermal hold at 1100°C for 1 hour (the vertical line at the right of each curve in Fig. 5), and the shrinkage was completed before cooling. Comparison of dilatometric results indicated that the higher green density gave the higher onset temperature for rapid densification. The temperature range of rapid densification was coupled with that of rapid grain growth. The final grain sizes were more than 500 nm for all three starting green densities as shown in Table 1 and Figure 6. It can be seen, however, that with the same sintering condition, there was a direct function between green density and final density, and an inverse relationship between green density and grain size, Figure 7. The higher the green density achieved, the finer the grain size and the higher the sintered densities were. In a green compact, the initial grain growth in a porous body (relative density<90%) is accomplished by coarsening of particles. Coarsening is also one of the mechanisms of reducing the pore coordination number to achieve densification. In order to achieve maximum densification with

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4 minimum coarsening during the initial stage of sintering, samples with higher green
5 density were favored. Thus, the higher the green density, the smaller the sintered grain
6 size because there was less coarsening needed for densification. With higher green
7 density, final densification can be completed at lower temperature and shorter times at
8 elevated temperature, which further suppresses grain growth.

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17 Due to the limits of current die design, higher pressures and temperatures have not
18 yet been tested for further increasing the green density of the nano W powders. However,
19 it is expected that the relative green density can be increased to greater than 70% at
20 pressing temperatures towards 700°C, which would make it possible to make ultrafine
21 pure W and nano W alloys following a simple press-sinter route.

22 23 24 25 26 27 28 29 30 31 **Summary**

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34 A warm compaction method for producing high density green parts of nanosized
35 tungsten powder was experimentally demonstrated. The concept was to use fine powders
36 from high energy ball milling, and to press green parts at temperatures high enough to
37 allow plasticity, but low enough to not incur excessive grain growth. The results
38 indicated ductile behavior initiating at 200-300°C for the nano-W powder compacts,
39 above which significant improvements in green density were achieved. For compaction at
40 450°C, a relative density of 58% was obtained, compared to 40% at room temperature.
41 This represents nearly a 50% increase over green compaction at room temperature.

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54 Sintering experiments performed in a dilatometer showed that under the same
55 sintering conditions (1100°C, 1h), there was a direct function between green density and
56 final density, and an inverse relationship between green density and grain size. In the
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most promising result, green compacts with ~55% relative density were sintered to 98% final density with an average grain size of ~585 nm.

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Table Captions

Table 1. Relative sintered density and W grain size of the nano-W with different green densities (~ 35%, ~45%, and ~55%), after sintering at 1100°C for 1 h in a dilatometer (theoretical density=19.25 g/cm³).

Figure Captions

Fig. 1. Schematic diagram for the high density green compaction technique.

Fig. 2. SEM micrograph of the high energy ball-milled nano W powder.

Fig. 3. Relative density of green compacts vs. applied pressure at room temperature and at 450°C.

Fig. 4. Effects of the pressing temperature and applied pressure on the relative density of green compacts of the nano-W powder; heating rate =10 °C/min, 1100°C, 1 hour.

Fig. 5. Dilatometric results of sintering nano-W compacts with different green density (relative density ~ 35%, 45%, 55%); linear shrinkage vs. temperature: heating rate =10 °C/min, 1100°C, 1 hour.

Fig. 6. SEM micrograph of the fracture surfaces of sintered nano-W. The initial relative green density was ~55%. Heating rate =10 °C/min, sintered at 1100°C for 1 hour.

Fig. 7. W grain size and relative sintered density vs. relative green density of nano-W powder.

Table 1. Relative sintered density and W grain size of the nano-W with different green densities (~ 35%, ~45%, and ~55%), sintered at 1100°C for 1 h in a dilatometer (heoretical density=19.25 g/cm³).

Relative Green density (%)	Relative Sintered density (%)	Sintered grain size (nm)
35.2	95.6	809±52
45.4	96.2	673±33
55.1	98.1	585±29

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Fig. 6. SEM micrograph of fracture surface of sintered nano-W. The initial relative green density was ~55%. heating rate =10 °C/min, 1100°C, 1 hour.

Fig. 7. W grain size and relative sintered density vs. relative green density of nano-W powder; sintered at 1100°C for 1 h in a dilatometer.