4.3 PROCESS IMPROVEMENTS FOR PREPARATION OF NANO-W SPECIMENS FOR MECHANICAL TESTING AND TESTING UNDER PLASMA ENVIRONMENTS— C. Ren and Zak Fang, Department of Metallurgical Engineering, University of Utah, 135 S. 1460 E. Room 412, Salt Lake City, UT 84112

OBJECTIVE

The objective of this work is to improve the fabrication process to minimize the grain growth while maximize sintered density. The nano-W specimens will be used to evaluate the mechanical properties and hydrogen permeation under plasma exposure conditions.

SUMMARY

In the last reporting period, the problem of sample cracking during sintering was resolved by implementing the novel multi-step pelletizing and compaction process (MPC). The ongoing work in this report period is focused on improving the sintered density of nano-W specimens. To accomplish this objective, a systemic study on the effect of sintering temperature, sintering atmosphere, sintering time and reduction temperature on the densification behavior of nano-W materials has been performed.

PROGRESS and STATUS

Introduction

For fusion reactor applications, the stability of the mechanical properties of plasma facing materials before and after irradiation is highly desired. Among various candidate materials, tungsten alloys is promising due to its superior mechanical properties with excellent thermal behaviors. [1-2]. In our previous work, we have developed processing method for making nano-W with grain size near 100 nm. [3-4]. However, when making large samples thye showed lateral and radial cracks after processing. In the last reporting periods, this cracking problem has been eliminated by introducing a novel multi-step pelletizing and compaction process (MPC). [5] The first set of specimens has been sent to our collaborator at Sandia National Laboratory (Dr. Buchenauer, Hydrogen & Metallurgy Science Department) for hydrogen permeation tests.

To further improve the mechanical properties and thermal behaviors of this material, the minimization of grain size and maximization of density of the sintered nano-W material is highly desired. Based on the last report, Ti-based additives work as pinning spots of grain boundary migration during sintering process which serves to minimize the grain growth of nano-W material. [5] The study further suggested that nano-W material with Ti additive has superior densification behavior than the material with TiC additive. The density of sintered nano-W increases as the sintering temperature increases. Based on these results, Ti has been selected as the additive for the further studies.

In this period, work to minimize grain size and increase relative density of sintered nano-W materials has been continued. The research work is mainly focused on the effects of processing parameters on the grain size and density of nano-W materials. The studied parameters include reduction temperature, sintering time, sintering temperature and sintering atmosphere. All of these parameters have been considered as factors that have significant effects on the densification of nano-W.

Experimental Procedures

<u>Green part preparation</u>
Commercial tungsten powders with particle size of about 100 nm and titanium hydride powders with particle size about 45 μm were milled using the customer designed high energy high pressure planetary mill (HEPM). The raw powders and 1 mm diameter tungsten carbide balls with ball to powder ratio of 4:1 were loaded in to the milling canister and then the canister was filled with mixed liquid of heptane and ethanol. The powders were milled for 6 hours and dried in evaporating dishes for 3 days. The dried tungsten powders were compacted to discs shape samples by the MPC process.

Low temperature sintering

A low temperature step was performed for 3 h to reduce the oxidized W powders and minimize its effect on sintering. The sintering steps were carried out at high temperature (above 1000 ºC) under hydrogen or argon atmosphere using a tube furnace. In this period of work, the reduction temperatures range is from 650 to 850 ºC, the sintering temperatures range is from 1000 to 1300 ºC and the sinter time range is from 1 to 16 h.

Characterizations

After sintering, the densities of samples were measured by Archimedes method. The fractured surface microstructures of sintered samples were examined by Scanning Electron Microscope (SEM). The surface areas of samples were characterized by Brunauer-Emmett-Teller (BET) surface area analysis method.

Results

Effect of sintering temperature, atmosphere and time

Ar and H_2 atmospheres and seven sintering temperatures range from 1000 to 1300 ˚C have been selected for comparison. The samples were prepared using MPC process, then low temperature reduced at 700 ˚C in H_2 for 3 h and high temperature sintered at the selected temperature with selected atmosphere for 1 h. Figure 1 shows the comparison of the effect of H_2 and Ar atmosphere on the densification of W - 1% Ti materials at different sintering temperatures.

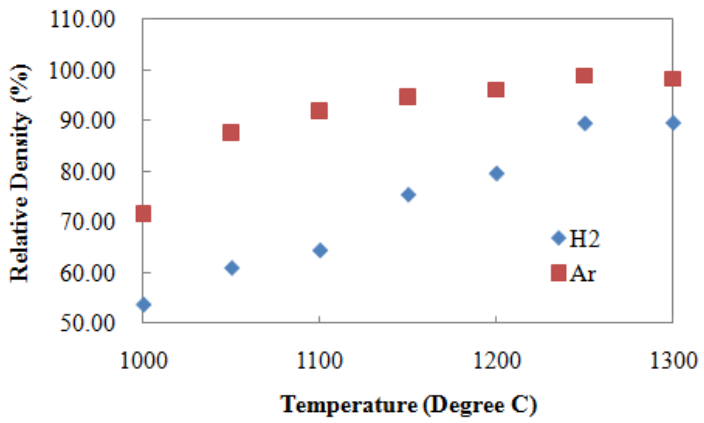


Figure 1. Comparison of W – 1% Ti sintered densities with Ar or H_2 atmosphere.

Similar to the data reported previously, the results demonstrate that the density of sintered W-1% Ti increases as the sintering temperature increases from 1000 to 1300 ˚C. Samples sintered in Ar atmosphere have higher relative densities than the samples sintered in H_2 atmosphere. This difference decreases as the temperature increases. The sample sintered at 1300 ˚C with Ar atmosphere has a density of 18.2 g/cc (relative density ~ 98.3%) which is the highest we obtained from this set of data.

To obtain better understand on the effect of atmosphere, a similar set of experiments were performed on the pure W samples. Figure 2 shows the comparison of the effect of H_2 and Ar atmosphere on the densification of pure W samples.

The results on pure nano-W has similar trend as the W – 1% Ti samples. Ar atmosphere sintering provides higher density than the H_2 atmosphere. The difference decreases as the temperature increases. The pure nano-W sample reaches a maximum density of 18.92 g/cc with 1300 ˚C sintering temperature and Ar atmosphere. Based on the result, this behavior arise from the interaction between W and H_2 gas. However, further study is required to obtaining better understanding.

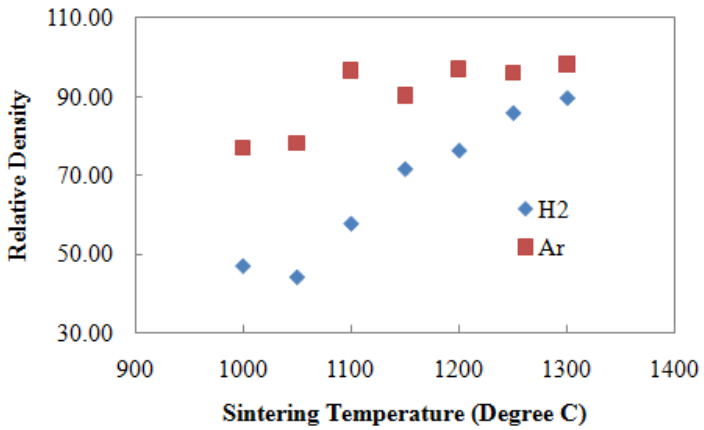


Figure 2. Comparison of W sintered densities with Ar or H_2 atmosphere.

Although high relative density is required for the structure material applications, a small grain size is also highly desired for the fusion reactor materials. Based on our study, a relative high sintering temperature (1300 ˚C) is required to reach the desired relative density. However, high sintering temperature leads to rapid growth in grain size which may decreases the mechanical property of nano-W. To investigate a potential solution to this problem, a study on the effect of sintering time on the densification of nano-W at relatively low sintering temperature has been performed. Figure 3 shows the relative density of nano-W samples sintered at 1100 ˚C in Ar atmosphere for 1 to 16 h.

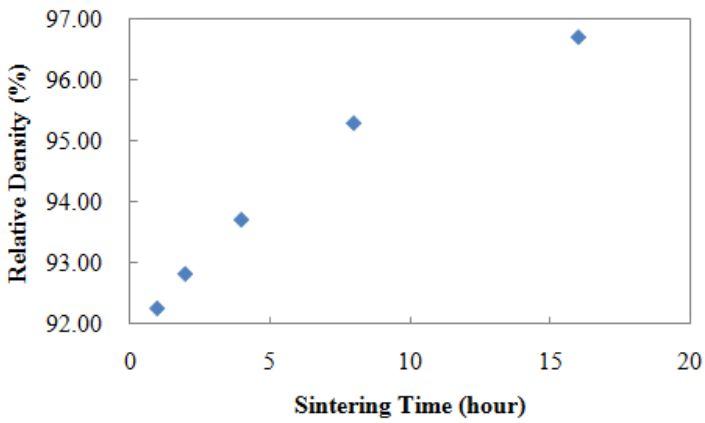


Figure 3. Effect of sintering time on densification of nano-W

As the sintering time increases from 1 to 16 h, the relative density of sintered nano-W increases from 17.1 g/cc (92.3%) to 17.9 g/cc (96.7%). This is about the same density as we obtained from high temperature sintered sample. However, a smaller grain size could be expected as the significant decrease in the kinetic of grain growth caused by the 200 ˚C decrease in sintering temperature.

Effect of reduction temperature

The effect of reduction temperature has been studied in the temperature range from 650 ˚C to 850 ˚C. After reduction, all of the samples were sintered in Ar at 1050 ˚C for 2 h and 1300 ˚C for 1 h. Figure 4 shows the results of the relative density of nano W – 1% Ti samples as a function of reduction temperature.

The result indicates the density of sintered W – 1% Ti first increases as the reduction temperature increases from 650 to 750˚C and then decreases as the temperature further increases to 850 ˚C. The W – 1% Ti sample reaches its maximum density at 700 or 750 ˚C.

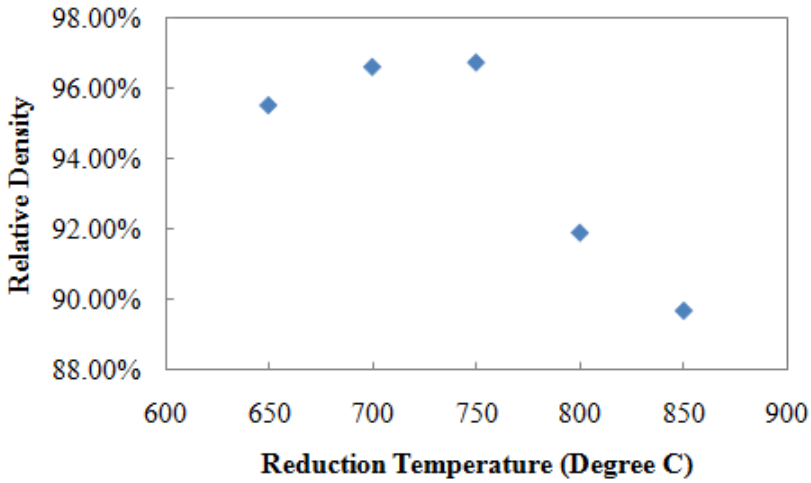


Figure 4. Comparison of W – 1% Ti sintered densities with different reduction temperatures.

To have better understanding on the effect of reduction temperature on the sintered density, similar experiments were performed on the pure nano-W materials. Figure 5 shows the comparison of the effect of reduction temperature on the densification of pure nano-W materials.

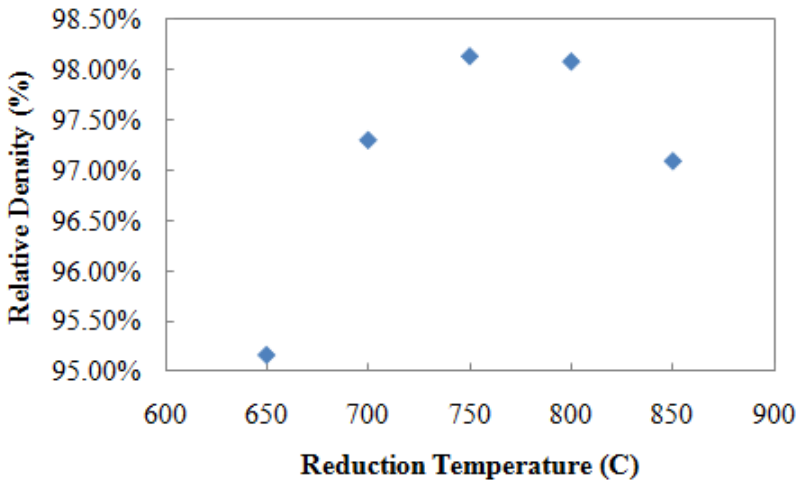


Figure 5. Comparison of W sintered densities with different reduction temperatures.

Pure nano-W has similar behavior as the W – 1% Ti material. As reduction temperature increases, the sintered density first increases and then decreases. Therefore, this behavior is also related to the W to H_2 reaction.

To minimized the potential effect of sintering on this reduction behavior, a set of pure nano-W samples were reduced at 650 to 850 ˚C and then directly cool down to room temperature without sintering step. Figure 6 shows the relative densities and surface area analysis results of these samples.

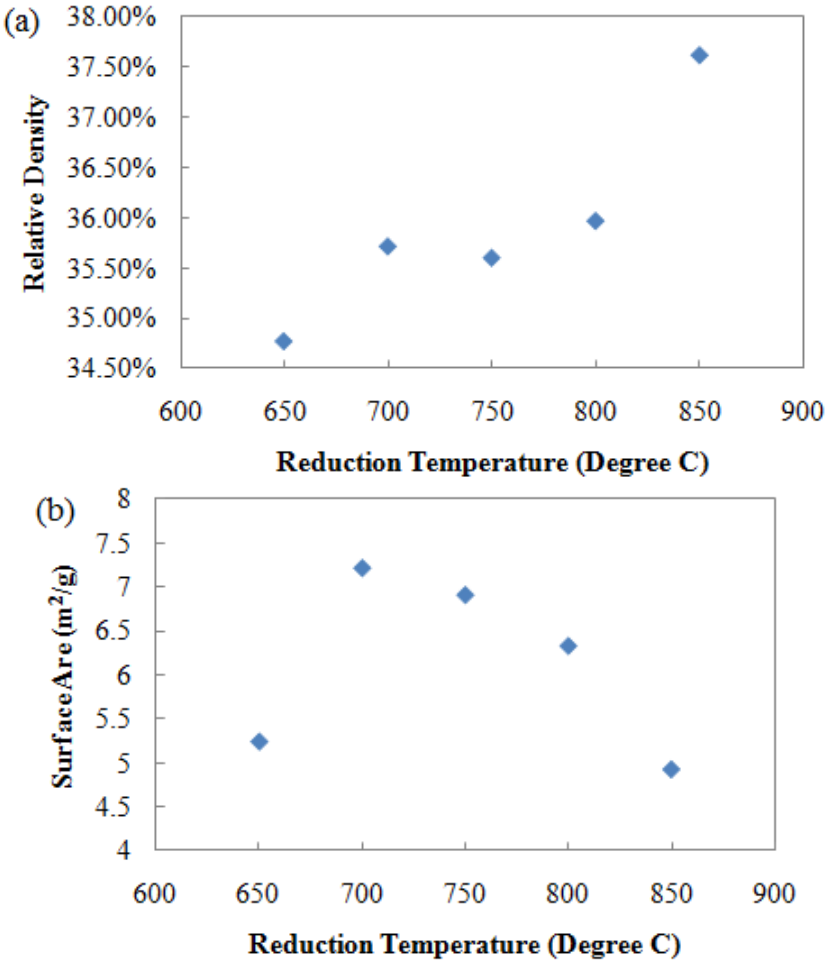
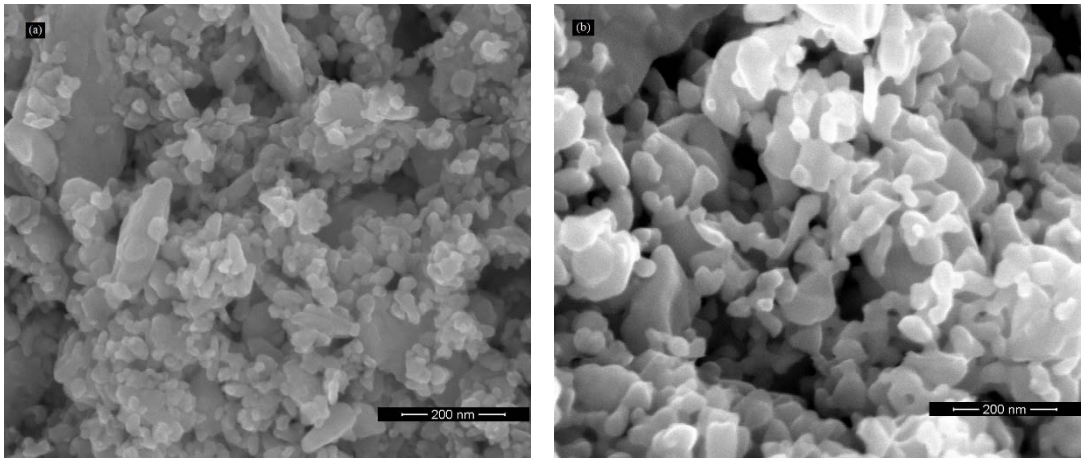


Figure 6. (a) Comparison of pure W densities after reduction at different temperatures.
(b) Comparison of pure W surface areas after reduction at different temperatures.

As shown in the figure, the relative density of reduced sample increases as the reduction temperature increases. The surface area density first increases as the reduction temperature increases from 650 to 700 ˚C which indicates a particle refinement effect. Above 700 ˚C, the surface area starts to decreases as a result of particle growth inside the sample. The surface analysis result has the similar trend as the sintered density data. As a result of the high activity of nano-sized W powders, pre-sintering effect may presents as the reduction temperature increases above 700 ˚C. This pre-sintering effect increases both the density and the grain size of the W samples. Figure 7 shows a microstructure comparison of samples reduced at 700 ˚C and 850 ˚C.



(a) (b)

Figure 7. Microstructure of pure nano-W samples reduced at (a) 700 ˚C and (b) 850 ˚C.

A clear difference could be observed on these two images, the particles reduced at 850 ˚C has smoother surface and necking starts to form between the particles. Based on the sintering theory, this pre-sintering step decreases the activity of nano particles and introduces necking which impendent further sintering process. Based on the result, 700 or 750 ˚C is the optimized reduction temperature which ensure the sufficient reduction of oxidize and limits the pre-sintering effect.

Future Work

Samples will be prepared with the optimized sintering process to obtain maximized relative density and minimized grain size. Further evaluation of mechanical properties and hydrogen permeation behavior will be performed.

Reference

[1] M. Rieth, et al, J. Nucl. Mater. 432 (2011) 482-500.
[2] M. Jain, et al, Int. J. Powder Metall. 42 (2006) 53.
[3] X. Wang, Z. Fang. Fusion Materials Semiannual Report DOE/ER-0313/53 (2013) 40.
[4] X. Wang, Z. Fang. Fusion Materials Semiannual Report DOE/ER-0313/54 (2013) 108.
[5] C. Ren, Z. Fang. Fusion Materials Semiannual Report DOE/ER-0313/55 (2015).