4.3 PROCESS IMPROVEMENTS OF SPECIMEN PREPARATIONS FOR MECHANICAL TESTING AND HYDROGEN PERMEATION OF NANO-W -- C. Ren and Z. Zak Fang (University of Utah)

OBJECTIVE

The objective of this work is to improve specimen preparation method to minimize cracking during abrication and optimize sample quality. The prepared nano-W specimens will be used to evaluate mechanical properties and hydrogen permeation for fusion reactor material applications.

SUMMARY

During the last period, attempts have been made to make crack-free specimens for mechanical and hydrogen permeation evaluations of nano W. The ongoing work in this reporting period including: development of a new multi-step pelletizing and compaction process (MPC) for preparing crack-free specimens, and evaluation of the effect of Ti-based additives on the sintering behavior of nano-W materials.

PROGRESS AND STATUS

Introduction

High performance mechanical properties before and after irradiation is the most desired characteristic for fusion reactor material applications. Among various materials, tungsten alloys with grain size less than 100 nm (Nano-W) is one of the most promising candidates due to its superior mechanical and thermal properties [1-2]. In our previous work, a new process method for making nano W with grain size near 100 nm has been developed [3-4]. This process method uses a “two-step” sintering strategy which includes a low temperature hydrogen sintering and a high pressure rapid heating modified rapid omni-directional compaction (m-ROC).

To further develop this material, large sample for mechanical properties evaluation is required. However, the large samples experience laminate and radial cracking as a result of the compaction introduced non-uniform density distribution. During the last reporting period, systematic studies on the effect of heating rate of sintering, compaction pressure, pressuring method and amount of binder have been performed on nano W materials. The results showed reduced formation of cracks by lower the compaction pressure and also suggested that the cracks were more likely to occur at lower density region.

In this period, work to eliminate cracks in sintered samples has been continued. Based on the experience of previous work, the cracking problem may be solved via obtaining green parts with more homogenous density. Therefore, the new MPC process has been developed which minimizes the density inhomogeneity and successfully eliminates formation of cracks.

To further decrease the grain size and increase the relative density of sintered nano W materials, effects of Ti-based additives on the sintering behavior have also been studied in this period. The parameters of

additive type (Ti and TiC), composition and sintering temperature have been considered as the most sensitive factors and may significantly affect the sintering results.

Experimental Procedure

Powder preparation

Commercial tungsten powders with particle size of about 100 nm and titanium hydride powders with particle size of 45 μm were used as raw materials. The powders were milled using the high energy planetary mill machine (HEPM) in a mixture of heptane and ethanol. One mm diameter tungsten carbide balls were used as grinding media with ball to powder ratio of 4:1. The milled nano tungsten powders were dried in evaporating dishes.

Multi-steps pelletizing and compaction process

The new MPC process is a solution developed during this reporting period which solves the cracking problem by minimizing the frictions between particles. The dried tungsten powders were compacted, pelletized, and re-compacted.

Low temperature hydrogen sintering

A low temperature step was performed at 700ºC for 3 h to reduce the oxidized W powders and minimize its effect on sintering. The sintering steps were carried out in temperatures range of 1000 to 1300ºC under hydrogen atmosphere using a tube furnace.

Characterizations

After sintering, the densities of the samples were measured by Archimedes method. The fractured surface microstructures of sintered samples were examined by Scanning Electron Microscope (SEM). Vickers hardness was measured under a load of 2 kg and a dwell time of 15 s.

Results

Disc specimen fabrication

To examine the radiation damage resistance properties, 1” thin nano-W disc specimens are required for the tritium permeating experiments. During the previous period, extensive works have been performed focusing on minimizing the formation of cracks during sintering. This part of work follows the previous efforts and by applying the new developed MPC process, the cracking problem has been solved.

Figure 1 compares the sintered 1” thick nano-W discs with and without MPC process. As shown in Figure 1 (a), a clear crack can be observed at the right side of the disc. Experimental result indicates that the crack is caused by the non-uniform green density throughout the sample. This non-uniform green density is formed by the friction between particles during compaction which is inevitable during traditional high pressure compaction process.

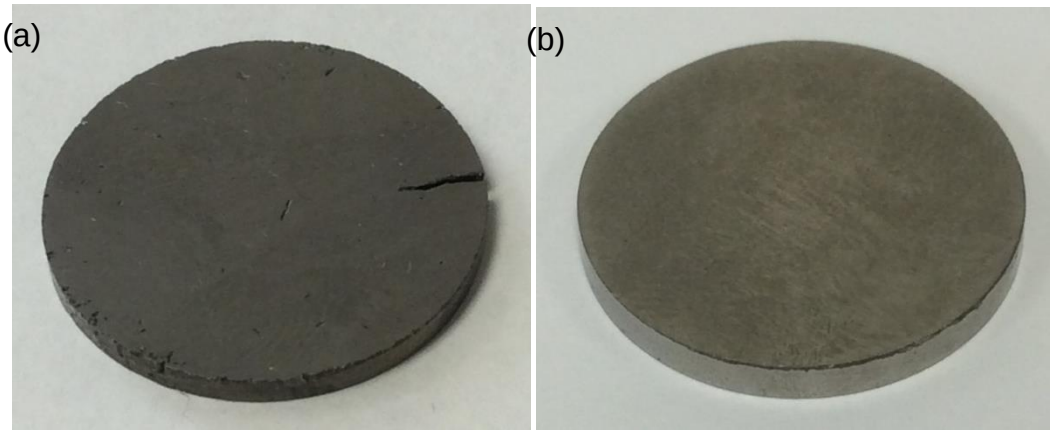

Figure 1. Nano W disc sintered at 1300 ºC for 1 hour. (a) Traditional compaction process. (b) MPC process.

The multi-step pelletizing and compaction process (MPC) offers a solution to achieve high green density while avoid causing high strain. During each compaction/re-pelletizing cycle, the long range macro strains are relieved by breaking the compact while high density are maintained inside each micro particles. Figure 1 (b) demonstrates a specimen prepared using the MPC process, no crack could be observed on the disc sample. The compacted sample has a relative green density of 34% which is comparable to the traditional method and could reach 97% relative density after low temperature hydrogen sintering.

Based on the results, the crack problem has been solved. Several high quality test specimens have been fabricated and one of them has been sent to our collaborator at Sandia National Laboratory (Dr. Buchenauer, Hydrogen & Metallurgy Science Department) for hydrogen permeation tests.

<u>Effect of additive type, composition and sintering temperature</u>

Two types of additive Ti and TiC have been selected for comparison. Figure 2 shows the relative density of W – x wt.% Ti/TiC (x = 0, 1, 2, 3.) samples. The samples were prepared by MPC process, then low temperature hydrogen sintered at 1050 ºC for 2 h and 1300ºC for 1 h. The pure W sample has the highest relative density of 98.1% and the relative density decreases as the composition of additive increases. Based on the previous research, Ti-based additives function as grain growth inhibitor during sintering of nano-W which keeps the grain size small and also decreases the relative density. Although small grain size is highly desired for fusion reactor applications, a very high relative density is required for structure materials. Based on Figure 2, at the same additive composition, nano-W with Ti additive has significant higher density than TiC additive. W with Ti additive also behaves less decrease in density as the additive composition increases. Based on this, Ti has been selected as better additive for further researches.

The effect of sintering temperature on relative density of nano-W has been studied by sintering a set of W – 1 wt.% Ti samples at 1000, 1100, 1200 and 1300 ºC for 1 h. As shown in Figure 3, a significant increase of relative density was achieved by increasing temperature to 1300 ºC. Relative density increases faster at

lower temperate and the rate becomes slower as the temperature higher. Relative density increased only 2% by increasing temperature from 1200 to 1300 ºC.

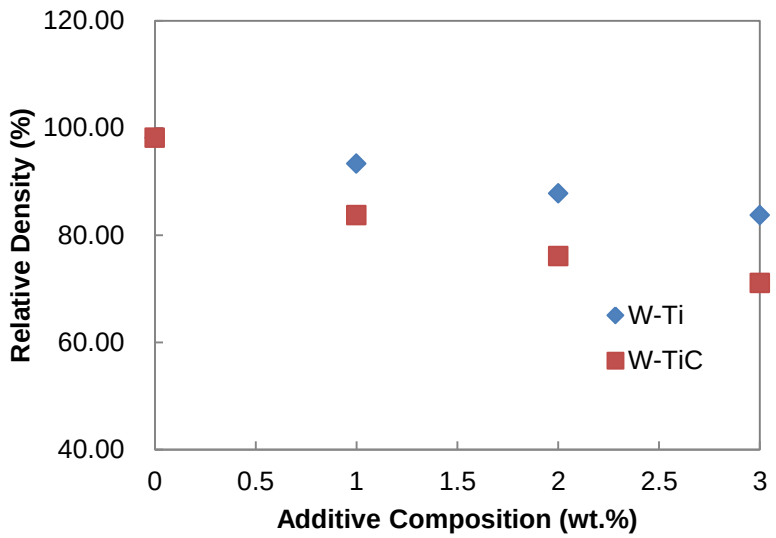

Figure 2. Effect of additive composition on densification of nano-W.

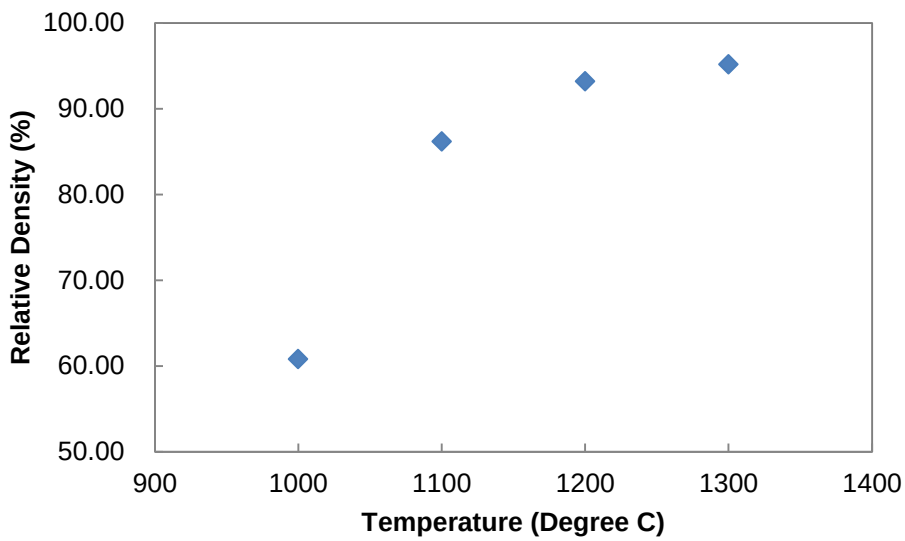

Figure 3. Effect of temperature on densification of nano W.

Samples of W – x wt.% Ti (x=0, 0.26, 1, 1.63, 2.7) have been prepared by sintering at 1100 ºC for 1h. The grain sizes are characterized using SEM on the fractured surface and the results are shown in Figure 4. As the Ti content increases, accompanied with decrease in relative density, a significant decrease is observed in the grain size of sintered samples. The hardness of the sample was determined using Vickers hardness test system. As shown in Figure 5, the HV value increases significantly as the Ti content increases and reaches a maximum of 1040 at the composition of W – 2.7 wt.% Ti.

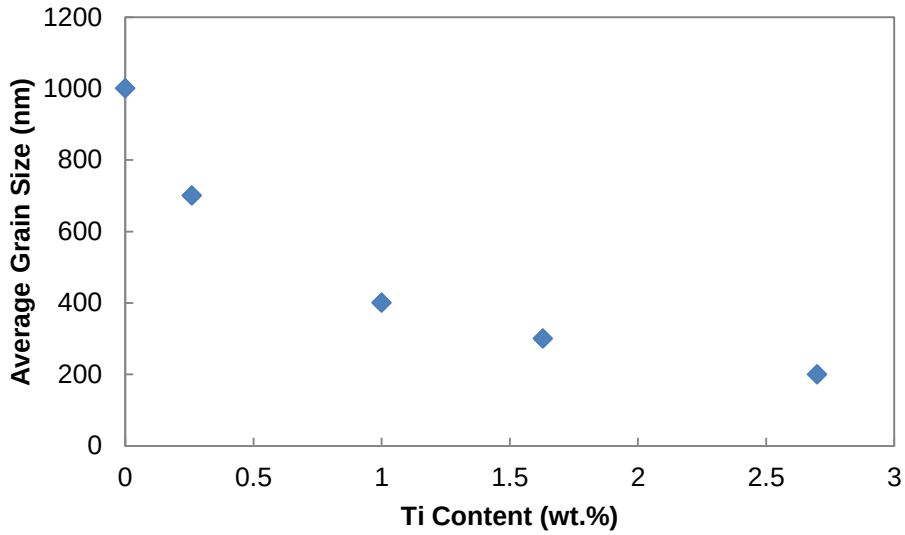

Figure 4. Effect of Ti content on grain size of sintered nano-W samples.

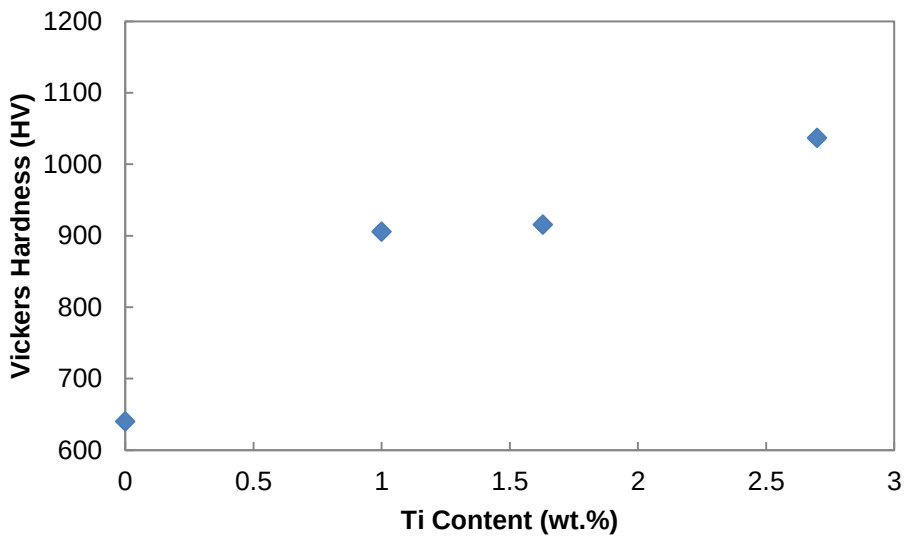

Figure 5. Effect of Ti content on hardness of nano W.

<u>Mechanism of additive effect</u>

To understand the mechanism of additive on nano-W's sintering behavior, SEM images had been taken on the W – 1 wt.% Ti 1300ºC sintered sample. Figure 6 shows one of the images taken at grain boundaries. EDS measurements have been performed on both phases which proved that the darker one is Ti and lighter one is W. Based on the image, a clearly tendency could be observed that Ti grains precipitates at the grain boundaries of nano-W which works as pin spots for grain boundary migration during sintering. This could explain the grain growth inhibitor effect of Ti-additives on sintering of nano-W.

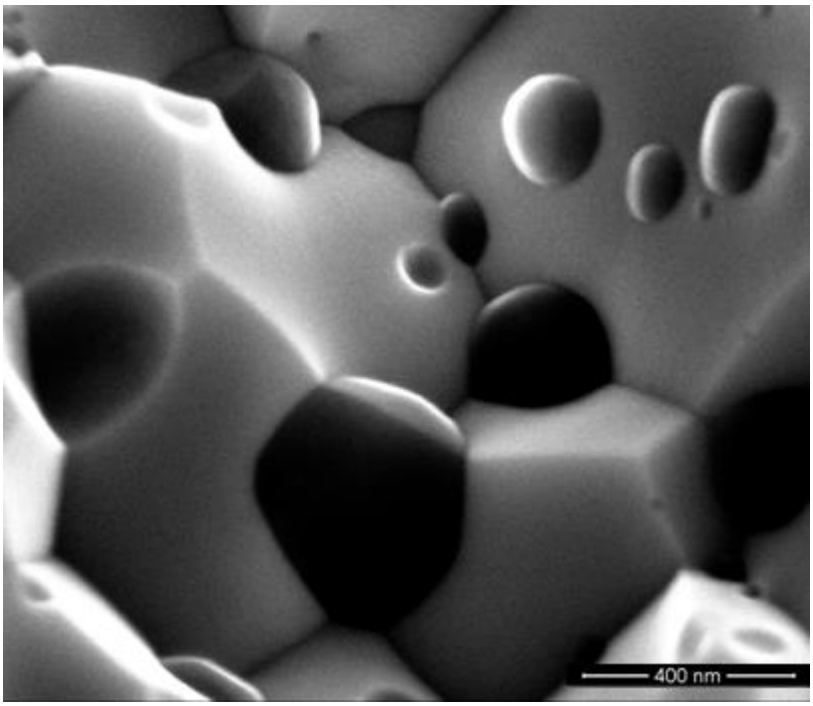

Figure 6. Microstructure of sintered W – 1 wt.% Ti sample at W grain boundary.

Future Work

The process will be further improved to obtain samples with optimized density and minimized grain size. Then the mechanical properties and hydrogen permeation behavior will be evaluated.

References

[1] M. Rieth, et al, J. Nucl. Mater. 432 (2011) 482-500.
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[3] X. Wang, Z. Fang. Fusion Materials Semiannual Report DOE/ER-0313/53 (2013) 40.
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