4.2 Effect of Ti and TiC Additives on Sintering Behavior of Nano W — X. Wang and Z. Zak Fang (University of Utah)

OBJECTIVE

The objective of this research is to evaluate the effect of Ti and TiC additives on grain growth and densification behaviors of nano W powders produced by a high-energy planetary ball milling process.

SUMMARY

Ti and TiC were added as grain growth inhibitors during sintering of nano W alloys. The sintering of nano W, W-1Ti, W-1Ti-0.5TiC, W-1TiC powders were investigated to understand the effect of Ti and TiC addition on grain growth and densification. The results show that both Ti and TiC can effectively prevent W grain growth during sintering. However, the additives also adversely affect densification. The combinations of Ti and TiC appear to have promise to be used for achieving high density while retaining nanoscale grain size.

PROGRESS AND STATUS

Introduction

Nanoscale grain structure holds promise for improving ductility and fracture toughness of tungsten, which is a candidate for structural applications in future, fusion reactors [1-4]. Significant efforts have been put into consolidating nanocrystalline tungsten powders [5-7]. However there remains the challenge of achieving full densification while retaining nanoscale grain size. Our previous work [8] has shown a high energy milled nano tungsten powder can be sintered to 99% relative density at 1100 °C, a significantly lower than normal temperature, under hydrogen; but the final grain size after sintering is larger than 2 micrometers, far beyond the nanoscale.

For controlling grain growth of nano W, grain growth inhibitors based on second phase particles and solute segregation has been introduced in literature. The addition of second phase particles such as La_2O_3 and TiC to tungsten impedes the mobility of the grain boundaries. Kurishita et al., reported that with addition of 0.5 % TiC, the grain size of a compact HIPed at 1350 °C can be as small as 50 nm with 94% relative density. The inadequate densification was due to low temperature of HIPing used in their study, which was necessary to suppress grain growth [9]. Recently, the mechanisms of grain refinement based on solute segregation received a lot of interest in the research community. Butler et al reported alloying with Zr and Hf for producing ultrafine tungsten [10]. More recently, Chookajorn et al., demonstrated a W-20 at%Ti powder with stable grain size of about 20 nm after holding at 1100 °C in Argon for a week [11]. They explained that in a nanoscale structure an unexpected heterogeneous chemical distribution for a bulk equilibrium alloy contributed to the stable nanostructure.

It should be noted that grain growth and densification of nano powders are often accomplished by the same diffusion mechanisms [12]. In many cases, inhibiting grain growth of a powder can drastically reduce the ability to achieve full densification due to reduced diffusion, which is necessary for densification. In the present research, based on our previous work, we are

engaged in a more in-depth study of doping nano W with grain growth inhibitors based on Ti and TiC and their combination, and study the correlations between the grain growth and densification versus the additions during sintering.

Experimental Procedure

Materials

Nano W, W-1Ti, W-1Ti-0.5TiC, W-1TiC powders were prepared by using a unique high-energy planetary ball milling (HEPM) process as illustrated in Figure 1. Our previous results have shown that the HEPM process significantly enhances the sinterability of the nanosized tungsten powders, achieving near-full density at much lower temperatures [8]. The powders were milled for 6 hours in heptane. Milled nano tungsten powders were compacted using a uniaxial press at 300 MPa. The green density was around 36% of theoretical density. Sintering experiments were carried out at temperatures between 950-1100 °C for 5 h in a hydrogen atmosphere using a tube furnace. Before sintering, the samples were reduced at 650 °C for 3 h in order to remove surface oxidation.

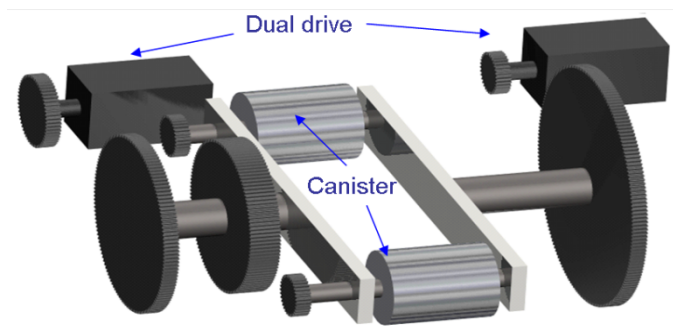

Figure 1. Schematic for the unique high energy planetary milling.

Characterizations

After sintering, the densities of the samples were measured by using Archimedes method. To take into account the influence of the initial as-pressed density, the sinterability of the powders can be expressed in terms of densification, which is calculated as follows:

$$Densification = \frac{Sintered \quad density - Green \quad density}{Theoretical \quad density - Green \quad density} \times 100\% \qquad (1)$$

The microstructural changes of the fractured surface of the sintered samples were observed using Scanning Electron Microscopy (SEM). Tungsten grain sizes were determined from the SEM micrographs by using the linear intercept method.

RESULTS

Milled Nano Powders

Figure 2 shows typical particle morphology of nano tungsten alloy powders produced by the high-energy planetary milling. The particle size of the most of the particles is in the range of 10–55nm. The average particle size is about 20 nm. It also shows that some particles agglomerate.

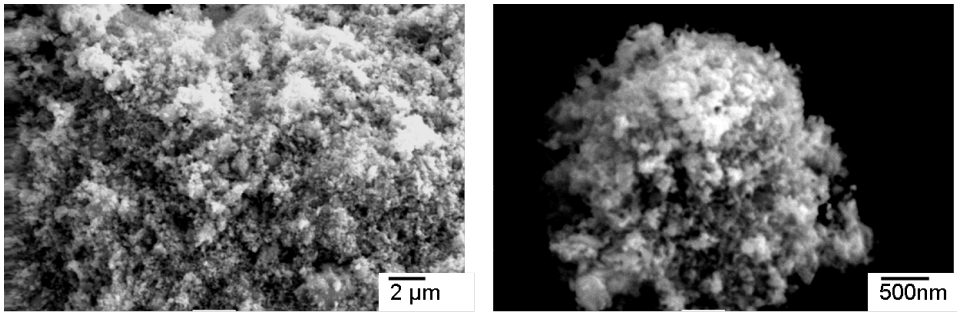

Figure 2. SEM images of high energy planetary ball milled nano W-1Ti powder

Microstructure Evolution versus Temperature

To study the effects of Ti and TiC additions on sintering behaviors of W, 4 nano powders of W, W-1Ti, W-1Ti-0.5TiC, and W-1TiC were sintered in the temperature range of 950-1100 °C. SEM microstructural examinations were conducted to observe the evolution of the tungsten grain structure vs. temperature for different powders, as shown in Figures 3-6. It can be seen in Figure 3 that W grains without any additives grow very rapidly with the increase of temperature, which is consistent with our prior results. In fact considerable WC grain growth occurred below 950 °C. At 950 °C, the W grains have grown to more than 100 nm. In contrast, Figures 4-6 demonstrates the addition of Ti and TiC to W grains effectively shifts the onset temperature of the W grain growth to higher temperature. Note that the temperatures for the surface morphologies of the W particles becoming smoothed and faceted were also delayed with the addition of the Ti and TiC.

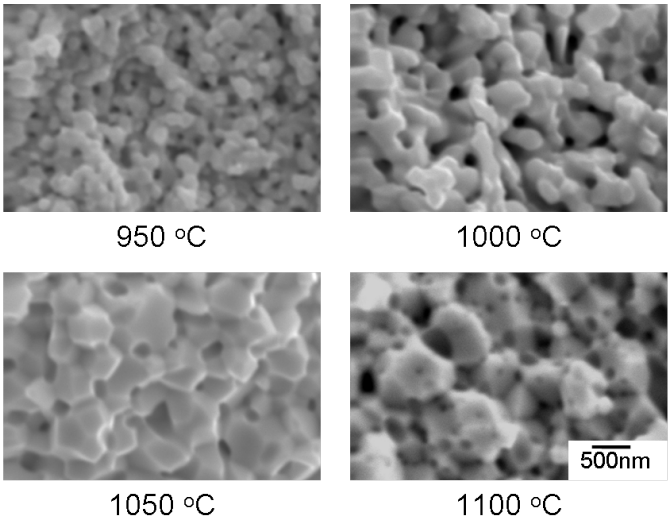

Figure 3. SEM images of fracture surface of sintered nano W at different temperatures.

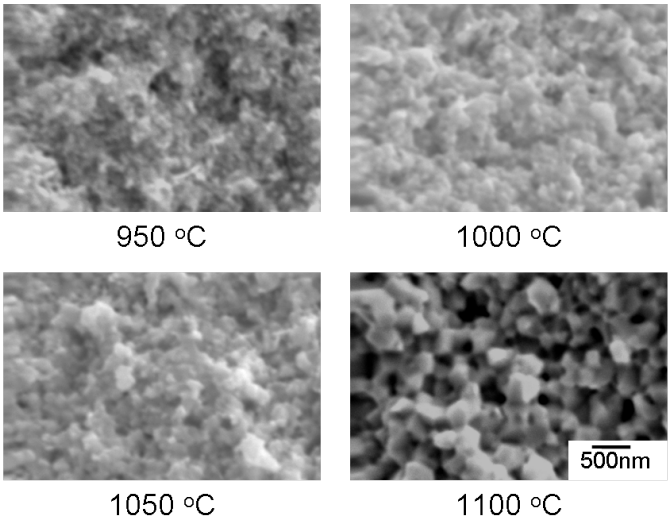

Figure 4. SEM images of fracture surface of sintered nano W-1Ti at different temperatures.

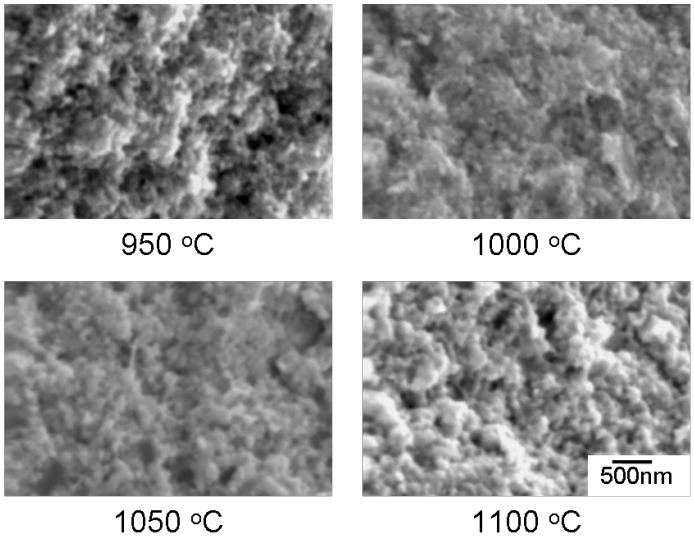

Figure 5. SEM images of fracture surface of sintered nano W-1Ti-0.5TiC at different temperatures.

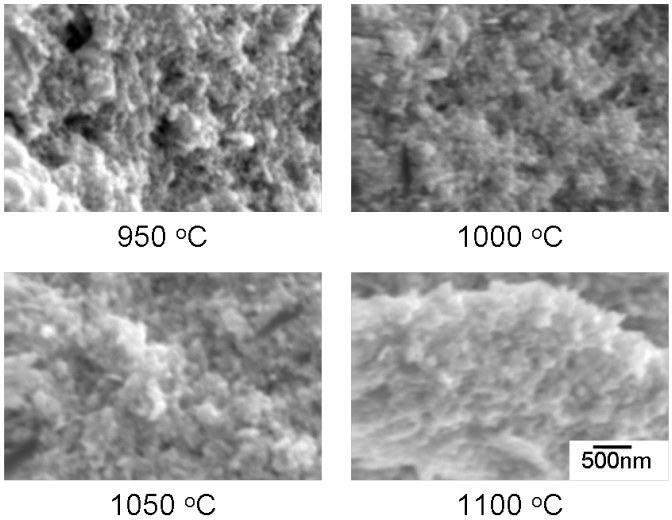

Figure 6. SEM images of fracture surface of sintered nano W-1TiC at different temperatures.

Grain Growth and Densification Behaviors

Figure 7 plots the W grain size and densification as function of sintering temperature between 950-1100 °C. It is obvious that the addition of Ti or TiC has significant effects on W grain growth and densification of the powders. According to the curves, both Ti and TiC results in low densification rate. 1 wt% of TiC severely retard the densification. When combined with Ti, 0.5 wt% of TiC shows little effect on the densification. As grain growth inhibitor, TiC is more effective than Ti. Ti is not so effective to limit the W grain growth in the intermediate densification stage when the temperature is over 1000 °C, probably due to Ti starts to facilitate the diffusion of tungsten. The grain size vs densification trajectories for the 4 powders were examined in Figure 8. The slope of the sintering trajectory of the W powder was significantly lowered with the addtion of Ti and TiC.

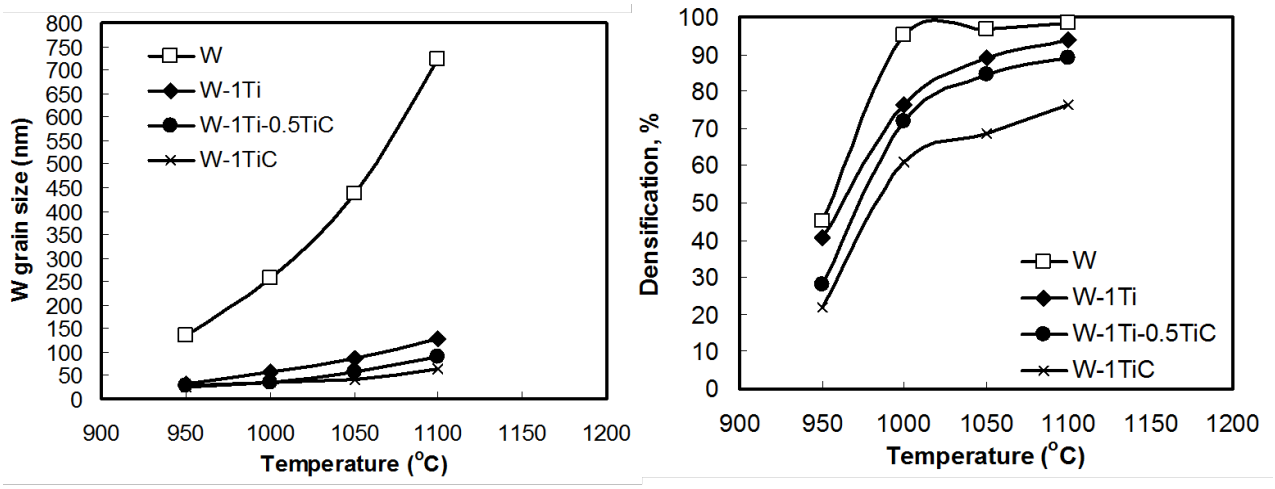

Figure 7. Grain size and densification as function of temperature during sintering of nano powders

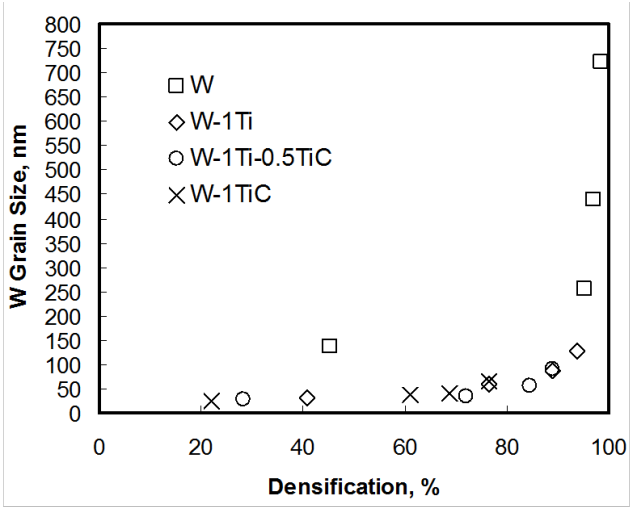

Figure 8. Grain size vs. Densification during sintering of nano W, W-1Ti, W-1Ti-0.5TiC, W-1TiC powders

Future work

The composition of W-Ti-TiC alloys will be optimized to achieve high density and minimized grain size.

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