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Development and Manufacture of Innovative Toughened Fine-Grained Recrystallized Tungsten Alloy

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Abstract. Tungsten (W) exhibits excellent thermal properties such as the highest melting point among the metallic elements, however, its engineering usefulness is limited due to the recrystallization embrittlement. Aiming at solving the recrystallization embrittlement, TFGR (Toughened Fine-Grained Recrystallized) W-1.1% TiC that exhibits high bending strength of 3.2~4.4 GPa and appreciable bend ductility at room temperature was developed. In collaboration with KEK, Sunric Co., Ltd., and Metal Technology Co. Ltd. (MTC) is upgrading the development phase for the engineering applicability of TFGR W-1.1TiC to increase the scale of manufacturing, to achieve mass production, and improve heat resistance and toughness. Reduction of gas-impurities such as oxygen and nitrogen is one of the essential factors in the manufacturing process. In this presentation, a fundamental study to understand outgassing behavior inside the HIP capsule will be introduced.

Introduction

Tungsten has the highest melting point at 3420℃ among the metal elements and a high density of 19.3g/cc. These properties have been attracting attention for use in high temperature environments due to its excellent thermal expansion coefficient being the smallest as well as high thermal conductivity. However, tungsten is a brittle material exhibiting low-temperature brittleness, recrystallization brittleness, and irradiation brittleness, so the engineering applications are remarkably limited. Though it is generally well known as a filament material for incandescent bulbs, the success of the present industrial fabrication of tungsten filaments required a variety of technological developments and efforts [1]. Tungsten has also been noticed as high heat flux materials and components of fusion reactors since the 1990's and it has been considered the most suitable candidate for this project. In 2008, Kurishita et al. of Tohoku University succeeded in developing a tungsten alloy TFGR that simultaneously improved low-temperature brittleness, recrystallization brittleness, and irradiation brittleness, which were the main disadvantages of tungsten [2]. The TFGR W alloy exhibits recrystallized nanostructures containing a high density of grain boundaries (GBs) of random orientations with high energies and nanoscale precipitation and segregation of transition metal carbides such as TiCx at the GBs. The precipitation and segregation at the GBs have the beneficial effect of significantly strengthening all of the GBs, suppressing the intergranular embrittlement (low-temperature embrittlement and recrystallization embrittlement). The prototype of TFGR was about 30mm in diameter. This small size continues

to place limits on industrial use. Makimura aimed at the application of TFGR to the large intensity proton accelerator target and the production of industrial volumes of TFGR became desired and a joint research project with MTC was established to carry out trial manufacture and mass production. Since 2017, MTC has installed a facility suitable for the process of powder preparation to sintering in order to produce TFGR industrial levels of production. The volume of toxic oxygen impurities during the process has been reduced as much as possible and a TFGR prototype was completed in 2019.[3] At present, the development of tungsten alloy is being promoted by constructing a project system with Sunric Co., Ltd. aiming at use in a wider array of industrial fields. This paper summarizes the present state of evaluating the oxygen concentration reduction measures. Oxygen concentration reduction measures are one of the most important points in the preparation of TFGR tungsten alloy.

Evaluation of oxygen concentration

TFGR W-TiC, which exhibits appreciable bend ductility even at room temperature, is manufactured in the following process such as; 1. Purification of powder without contact with oxygen and nitrogen during handling of the powder, 2. Mechanical alloying (MA), which is carried out in a vacuum vessel with balls with W-TiC powder to refine crystal grains of W-TiC to W matrix, sintering at a low temperature as possible to keep the grain-size refined, 3. Microstructural modification by grain boundary sliding (GSMM: Grain boundary Sliding-based Microstructural Modification) to promote grain boundary segregation and precipitation of TiC in the W matrix [2]. At the time of implementing all the measures examined as the measure of the O2 level, the oxygen level after hot isostatic pressing, was 240ppm (wt. ppm). In order to reduce the DBTT (Ductile-Brittle Transition Temperature) in the three-point bending test to room temperature or lower, the target oxygen concentration is 450ppm or lower.

Degassing equipment

Mixing and degassing of W powder and TiC powder, loading and unloading of powder into and out of the MA container, filling the HIP capsule, and welding are all carried out inside the glove box (GB). The GB is filled with an inert gas, argon (Ar), and the oxygen concentration is kept at 1ppm or less by an Ar gas circulation purifier at all times. A vacuum chamber for heating and degassing is attached to the side of the glove box. A special welding machine is connected to weld the HIP capsules (Fig.1). The vacuum chamber for heating/ degassing is supplied with a door for manual access from within the GB. A turbo molecular pump, TMP, and a dry pump are used for the vacuum exhaust and a quadrupole mass spectrometer, Q mass, is mounted for analysis of the exhausted components.

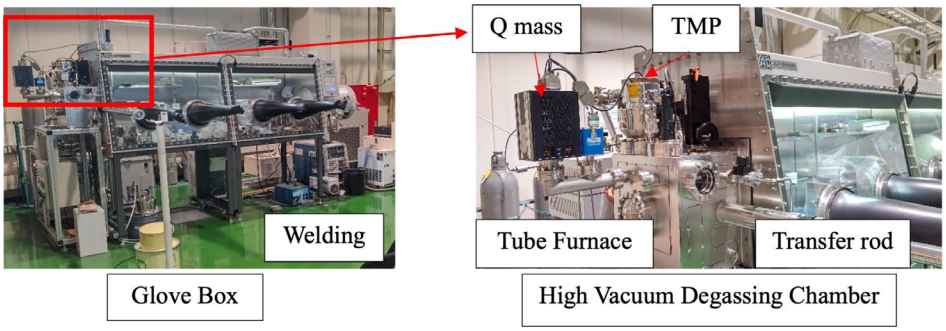

Figure 1. Pictures of the glove box: OMNI-LAB (VAC), vacuum chamber, a TMP pump: TG350F (OHSAKA VAC), a tube furnace: TMF700N (AZONE) and a Q mass: HPS2 (MSK).

Pass boxes are used for taking objects in and out of the GB while the atmosphere is replaced by Ar gas in a vacuum and the low oxygen state is always maintained. The vent line of the vacuum chamber uses Ar commonly circulated in the GB. The overall system diagram is shown in Fig. 2.

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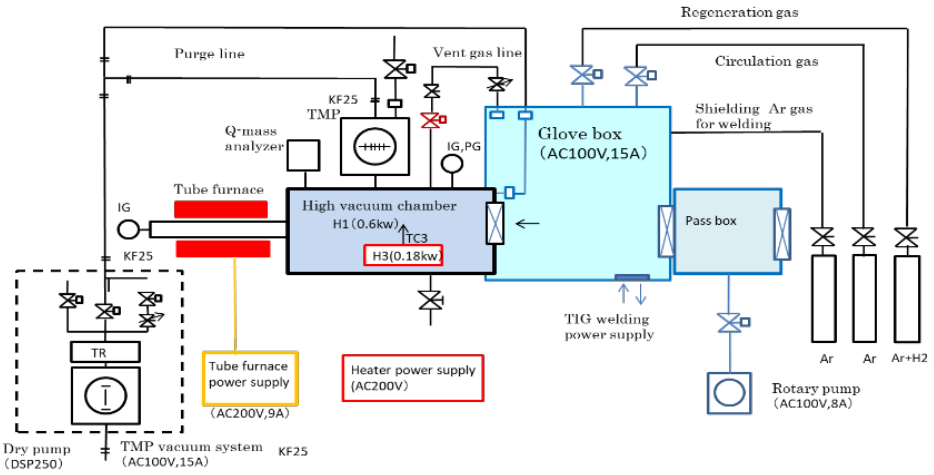

Figure 2. Schematic Diagram of GB, High Vacuum Chamber, Tube furnace

Degassing

Mixing of the powders is carried out in the GB using an electronic balance. The blended powder is placed in a tantalum, Ta boat and attached manually to the tip of the high vacuum chamber in an Ar atmosphere in the GB. The powder is evacuated from the chamber and moved to the vacuum tube furnace by a transfer rod. Degassing is carried out at 950℃ for 1 hour. After degassing, only the powder is placed into the MA vessel containing the balls for MA which is in a high vacuum chamber. The lid of the MA container attached to a vertical drive shaft is lowered with the transfer rod, then the vacuum chamber is vented, and the container is sealed by vacuum load against atmospheric pressure. Finally, bolts are inserted into the through-holes of the container in the GB. The heated degassing and high vacuum chambers can be seen in Fig. 3.

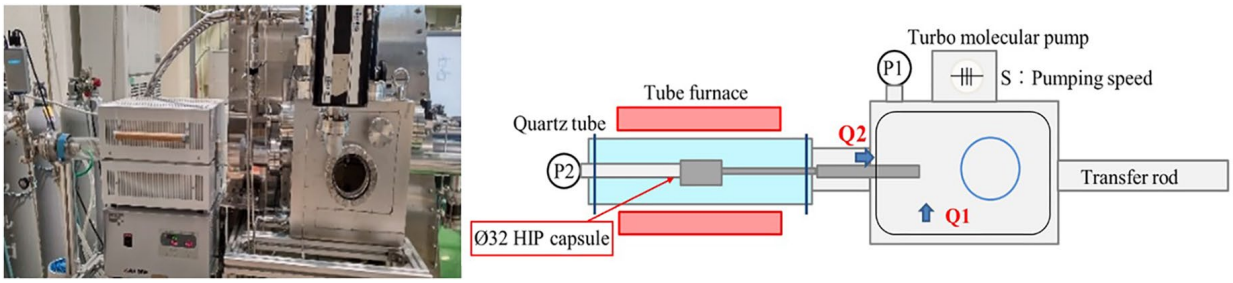

Figure 3. Photographs and Block Diagrams of Heated Degassing and High Vacuum Chambers

HIP Capsule Welding/ Degassing Treatment

The MA powder is packed in a HIP capsule in the GB, then the capsule with a pipe is enclosed through TIG welding the HIP capsule and is placed under a vacuum while heated to eliminate residual gas. Ar gas that creates an inert atmosphere to ensure a stable TIG discharge is supplied separately. A leak test is performed after welding using the exhaust port in the GB. Thereafter, the HIP capsule and the powder is heated and degassed in the tube furnace. Finally, the pipe for pumping is pinched and welded to realize sealing. A schematic of the HIP capsule can be seen in Fig. 4.

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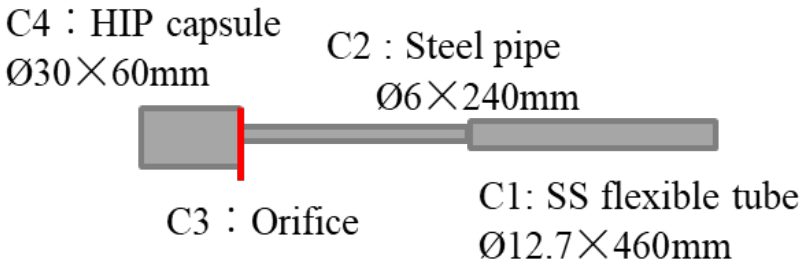

Figure 4. HIP-Capsule and Pipe Schematic Drawing

Conductance of powder inside HIP capsule

So far, it was verified that the powder filling and degassing in the HIP capsule were sufficiently carried out. When the capsule is pumped through the pipe, the vacuum pressure at the bottom of the HIP vessel depends on the conductance of the powder. According to previous literature [5], the conductance through the powder has been measured for viscous and molecular flows in a relatively low vacuum. The conductance depends on the vacuum pressure, and in both cases, it is proportional to the cross-sectional area of the pumping path and inversely proportional to its length. In this study, the vacuum pressures at the bottom of the HIP vessel and at the vacuum pump position were measured to estimate the amount of degassing and the conductance in high vacuum. Degassing rate of the stainless steel and the quartz can be assumed from the handbook of the vacuum science. The amount of total degassing can be estimated by multiplying the surface area of the vacuum chamber of the stainless steel and the surface area of the quartz tube furnace. From this degassing quantity and the pumping speed from the turbo molecular pump, the vacuum pressure was predicted and the comparison with the measured value was carried out (Table 1). Furthermore, the conductance can be estimated from the diameter and length of the piping and the HIP capsule. As the result, it was confirmed that the prediction is consistent with the measurements for the empty HIP capsule that does not contain powder (Table 2).

Table 1. Confirm of Attained Vacuum

Pumping speed of turbo pump	310	L/sec
S: Effective pumping speed	0.295	m^3/s
Q1: Outgassing from chamber	9.94×10^{-6}	Pam^3/s
Q2: Outgassing from tube furnace	9.15×10^{-7}	Pam^3/s
Ultimate vacuum (Q1+Q2)/S	3.68×10^{-5}	Pa
Measured value	4.50×10^{-5}	Pa

Calculated Pressure	Measured Pressure
P1: 3.74×10^{-5} Pa	P1: 4.5×10^{-5} Pa
P2: 4.22×10^{-3} Pa	P2: 8.5×10^{-3} Pa

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Table 2. Conductance and outgassing of HIP capsule + pipe.

Conductance

C1: SS flexible tube	5.39×10^{-4} m^3/s
C2: Ø6 Steel pipe	3.23×10^{-5} m^3/s
C3: Orifice	1.16×10^{-4} m^3/s
C4: HIP capsule	5.45×10^{-2} m^3/s
C capsule: Total conductance	2.41×10^{-5} m^3/s

Outgassing

q1: SS flexible tube	4.04×10^{-10} m^3/s
q2: Ø6 Steel pipe	3.32×10^{-8} m^3/s
q3: HIP capsule	6.74×10^{-8} m^3/s
qT: Total outgassing	1.01×10^{-7} m^3/s

The amount of outgassing from the powder was estimated from the vacuum pressure P1 near the turbo-molecular pump and the pumping speed by putting the powder into the HIP capsule afterwards. Then, the conductance was determined from the differential pressure of the vacuum pressure P2 at the bottom of the HIP capsule and P1. A quadrupole mass spectrometer, Q mass, was used to identify the types of gas released when the HIP vessel with a diameter of 32 mm and the powder were degassed (Fig. 5).

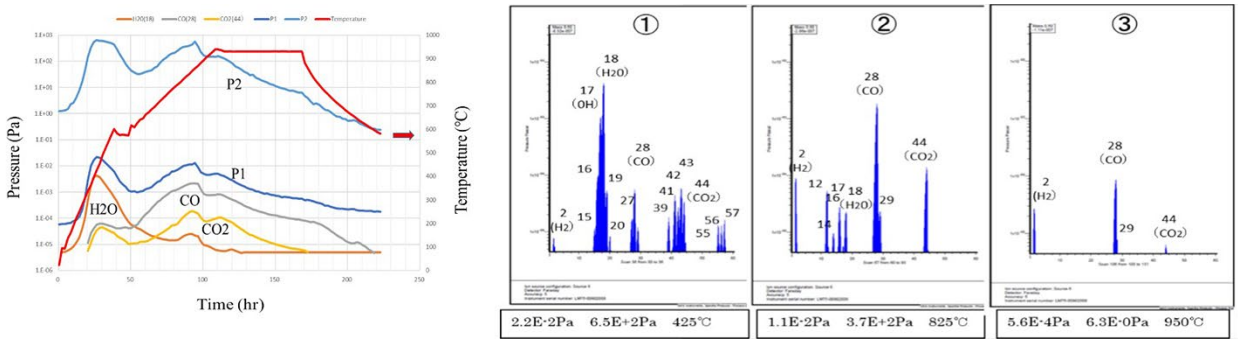

Figure 5. Degassed Properties with Powder and Q mass Spectral Data at Elapsed Time Points ①②③

From the differential pressure, the conductance after degassing of the powder was calculated that at a diameter of 32mm capsule was 2.56×10-4Pam3/s (Table 3). It was confirmed that the HIP capsule bottom was exhausted to 1.3 × 10-3 Pa even when the HIP capsule was considerably packed with powder.

Table 3. Powdered Vacuum and Powder Conductance Calculations

P1(measured)	1.60×10^{-4}	Pa
P2(measured)	1.30×10^{-1}	Pa
Outgassing Qt = P1×S	4.72×10^{-5}	Pam^3/s
Amount of gas other than powder Q0	1.10×10^{-5}	Pam^3/s
Amount of gas from powder Qp = Qt-Q0	3.62×10^{-5}	Pam^3/s
Outgassing from HIP capsule and pipe Qh	1.01×10^{-7}	Pam^3/s
Conductunce of powder (Qp+Qh)/(P2-P1)-Ct	2.56×10^{-4}	m^3/s

Discussion

It was verified that the specifications required for the fabrication of TFGR W alloys were satisfied in the present pumping system. Subsequently, the largest dimension that can be introduced into the tube furnace is 50mm in diameter. It was confirmed that the conductance is $8.66\times10^{-4}Pam^3/s$.

Degassing rate of W powder. The degassing rate of W powder was calculated from the total amount of outgassing and powder from the measured W powder of 200g. Assuming the powder particle diameter as a sphere of 2μm, the weight of one particle is determined to be $8.0\times10^{-11}g$. The volume of W powder in the HIP capsule is 200g, then the number is 2.49×10^{12}. The surface area of the particle is $1.26\times10^{-7}cm^2$ assuming a spherical shape, and the total surface area is $9.42cm^2$. Dividing the degassing amount of the powder 3.5×10^{-5}Pam3/s by the surface area becomes $1.12\times10^{-6}Pam^3/s/m^2$. This value is close to the normal metallic surface (e.g., SS304) and looks reasonable.

Conductance of gas permeating W powder. The conductance of the powder–filled in HIP capsule was calculated to be $2.56\times10^{-4}m^3/s$. For comparison, we calculated the diameter to be 4.7mm if this conductance were in the shape of a pipe and length were 50mm. This diameter was larger than expected. It is presumed that the reason for this result was that the powder had a large conductance. As a results, the pressure of the bottom of the HIP capsule was lower than expected.

Summary

Though the production of TFGR W alloy prepared until now by MTC is not yet at a mass production level, it was judged that the basic parameters required for manufacturing larger sizes has been confirmed.

- Treatment of all powder handling without touching the atmosphere resulted in a 240ppm oxygen-concentration for TFGR W alloy fabrication (must be less than 450ppm) [4].
- The vacuum at the bottom of the HIP capsule reached 1.3×10^{-1} Pa using the degassing process for the HIP capsule even when the W powder was packed. When the pressure of P1 entrance of HIP capsule was 1.60×10^{-4}Pa which was two orders of magnitude smaller than the bottom value.
- Analysis of the Q mass in the degassing step of the W powder at 950℃, it was confirmed that the peak of the CO is present even after 1 hour has elapsed. In this degassing system, it is considered that the oxygen concentration is further improved by treatment at high temperature for a longer period of time.

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