Interface interaction of tungsten film deposited on glassy carbon under vacuum annealing

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Highlights

• The deposited W film on glassy carbon is smooth and featureless.

• W protective films on glassy carbon are stable up to 700 °C.

• Reaction zone observed to grow wider with increase in temperature.

• Rough surface appear at 800 °C and the feature increases with temperature from 900 to 1000 °C.

Abstract

Thin films of tungsten (W) were deposited on glassy carbon substrates using magnetron sputtering system. The as-deposited samples were annealed under vacuum at temperatures ranging from 600 to 1000 ^{o}C for 1 hr. The interface interaction of W and glassy carbon was investigated by Rutherford backscattering spectroscopy (RBS) and scanning electron microscopy (SEM). RUMP software was used to simulate the RBS spectra. The thickness of W thin film deposited, atomic composition of deposited layer and the reaction zone (RZ) were deduced from the RUMP simulation results. The surface morphology of the diffusion couples were examined using SEM. The as-deposited sample possessed a smooth uniform layer of W film while the annealed samples showed a progressive increase in surface roughness with increased annealing temperature. The stability of W-glassy carbon diffusion couple under heat treatments suggests that it might be useful for long-term structural integrity of dry cask storage devices and in general applications where a radiation shield is required

Keywords: glassy carbon, tungsten, interaction, RBS, SEM

1. Introduction

Carbon belongs to a remarkable class of materials with combined properties such as low density, high strength, hardness, or, elasticity because of the flexibility to form sp^1-, sp^2-, and sp^3-hybridized bonds [1]. Carbon exists in the form of many allotropes. In its natural form, carbon exists as amorphous carbon, graphite and diamond; carbon also exists in synthetic form as glassy carbon, fullerene, graphene, carbon nanotube and more recently as carbyne which is believed to be the strongest material in the world [2].

Glassy carbon is a synthetic form of carbon which combines glassy and ceramic properties with those of graphite. It is a stable material which does not graphitize even at high temperatures up to 3000 ^{o}C [3]. Glassy carbon exhibits attractive physical, chemical and mechanical properties which make it very promising for technological applications [4]. These properties include moderate hardness, resistance to corrosion and wear, high chemical inertness [5], impermeability to gases and liquids [6], high temperature stability, high thermal conductivity, good resistance to thermal shock and low coefficient of thermal expansion [7]. These properties make glassy carbon more useful for many industrial applications such as vacuum evaporation sources, radiation containment, zone-refinement crucibles and encapsulation of spent nuclear fuel.

Tungsten (W) is a heavy metallic element**,** a member of the third series of transition metals. Tungsten has the highest melting point of all metals, and at temperatures over 1650 °C has the highest tensile strength [8]. It has good chemical, physical and mechanical properties; such as high thermal conductivity, irradiation resistance, exceptional corrosion and abrasion resistance. W also exhibits a low sputter rate and good thermal conductivity [9]. Due to these excellent properties of W, it can serve two main applications in the nuclear waste storage system. Firstly, it can act as shield component due to its low sputter yield and, secondly, it is expected to provide structural enhancement due to its high strength.

Storage and containment of nuclear waste is a major scientific challenge in nuclear energy which has adversely affected the acceptability of this form of energy by the general public due to safety concerns. Currently, glass materials are being used for encapsulation of nuclear waste in solid form [10]. This waste is then stored in dry cask storage containers which are meant to be temporary until they are transferred to permanent geological sites. Demand for dry casks with

longer service lifespan than they have nowadays, is expected to be on the increase in the near future due to the dearth of permanent repositories. Currently, dry cask storage devices with expected lifetime of 40 - 50 years, which are made from materials such as stainless steel, cast iron and concrete are being used to contain nuclear waste. The problems with these materials are their susceptibility to corrosion and chemical attacks, which could result to leakage thereby posing serious threats to man and the environment. Therefore, there is need for intensive research towards improved service and longevity of dry casks for nuclear waste storage.

The excellent properties of glassy carbon have drawn the attention of many researchers to conduct study on its performance improvement by ion implantation coupled with annealing. Notable studies on ion species implanted in glassy carbon include Cd [3], In [4], Cs [11], Sr [12] and the results showed that the diffusion patterns of the implanted fission products are not into the bulk of the glassy carbon but rather towards the surface damaged by the ion implantations. Results from these previous studies suggested that glassy carbon has promising stability in a radiation environment. Our literature search revealed that no study of W deposited on glassy carbon has been investigated. In this investigation, the choice of W is meant to complement the radiation shield ability of glassy carbon noting that low Z atoms provide poor shield to high gamma rays. Elements with high atomic numbers, of which W is one, provide good shields to radiation especially the gamma rays due to their massive nuclei [13]. In addition to this, W also possesses high strength and thermal conductivity which can augment the structural strength of the cask and reduce heat build-up within the storage device. In light of the foregoing, this study focuses on investigating the stability of the W-glassy carbon matrix resulting from the solid state interaction between glassy carbon and W interface under vacuum annealing.

2. Experimental Method

The starting materials were rectangular strips of glassy carbon with dimensions of 50mm × 10mm × 2mm. The glassy carbon strips were obtained from a popular glassy carbon manufacturing company known as Hochtemperatur-Werkstoffe GmbH, in Germany. According to the company [14], the glassy carbon grade SIGRADUR® G has a density of 1.42 g/cm^3, flexural strength of 260 MPa, compressive strength of 480 MPa, Young's modulus of 35 GPa, thermal conductivity of 6.3 W/m.K (at 30°C) and maximum service temperature up to 3000 ^{o}C.

Glassy carbon strips were cut into smaller size of 5mm × 10mm × 2mm and thereafter polished on a Saphir 500 polishing machine for 5 minutes using diamond suspension and silica gel of 0.25 µm and 0.5 µm, respectively. The polished samples were then cleaned with de-ionized water and methanol and then dried in an oven at 40 ^{o}C for 10 minutes. Diffusion couples comprising W films and glassy carbon substrates were made by physical vapour deposition method using the magnetron sputtering system. An average deposition rate of 1.03 nm/sec was estimated for depositing the desired W film thickness. Glassy carbon substrates were first mounted on a cleaned circular sample holder with area of 78.5 cm^2, which was then mounted in the chamber of the magnetron sputter system. The distance between the substrate and tungsten target was approximately 20 cm. The chamber pressure was first pumped down to 10^{-5} mbar and argon gas was introduced into the chamber with its pressure adjusted to 10^{-3} mbar giving rise to gaseous plasma in the chamber when the magnetron was switched on. The surface of W target was etched by Ar plasma for 5 minutes to ensure that any contaminant on its surface was removed before the actual sputtering process was carried out at room temperature. The sputtering parameters were carefully optimized after several attempts to ensure good adhesion between the W film and glassy carbon substrates. The magnetron was powered by voltage of 500 V and with the current adjusted to 0.28 A on the magnetron, the working power of 140 W was used to carry out the sputtering. Under this low power condition, it is not expected that the temperature of the substrates would rise significantly, at least not to a level where phase reaction would take place.

The W-glassy carbon diffusion couples were annealed in vacuum using a tube furnace annealing system. High vacuum annealing was performed on the as-deposited samples for 1 hr each with temperatures ranging from 600 to 1000 ^{o}C with a step interval of 100 ^{o}C. A hollow tube furnace was used to anneal the samples which were mounted inside a separate hollow quartz tube. The furnace was switched on while the quartz tube was being vacuum pumped down, simultaneously. When the furnace reached equilibrium at the required annealing temperature, the quartz tube was quickly inserted into the opening of the furnace resulting in quick heating of the samples. Typically, it took about 5 – 10 minutes for the samples to reach the annealing temperature. At the end of annealing period, the quartz tube was quickly pulled out of the furnace, allowing the samples to cool down to room temperature. The cooling rate constant according to Newton's law of cooling [15] was estimated as 0.06 min^{-1}. After each isochronal annealing, the vacuum tube

containing the sample is allowed to cool down to room temperature before unloading the samples; this ensured that oxidation of W film is minimized as low as possible.

All the annealed and as-deposited samples were analysed using the Rutherford backscattering spectrometry (RBS) system and the results were simulated with RUMP software. RBS analysis was performed using He^+ ions at incident energy of 1.6 MeV, beam current of 15 nA, backscattering angle of 165^o, detector resolution 15 keV and collected charge of 8 μC. The thickness of W layer deposited, atomic composition profile as well as information indicative of intermixing across the interfaces of the diffusion couples were extracted from the RBS-RUMP simulated results. A scanning electron microscopy (SEM) powered by a Zeiss Ultra 55 high resolution field emission microscope was used to examine surface morphology of all the samples before and after annealing.

3. Results and Discussion

The RBS spectrum of as-deposited sample is shown in Fig. 1 together with the RUMP simulated spectrum. The simulated spectrum is shown as a red line while the black one is the experimental RBS result. The arrows in Fig. 1 indicate the surface channel positions of W and C at channel numbers 473 and 122, respectively. With the aid of RUMP simulation, the thickness of W film deposited on glassy carbon substrate was estimated to be 392×10^{15} at./cm^2 (i.e. 62 nm). Elemental composition of the deposited film was found to comprise 91.8 at.% W and 8.2 at.% O, thus showing the presence of impurity oxygen in the W film. The low energy edge of the W peak and carbon high energy edge were observed to be almost flat. This indicates that the interface between the W film and glassy carbon substrate was sharp and no diffusion had occurred during W film deposition.

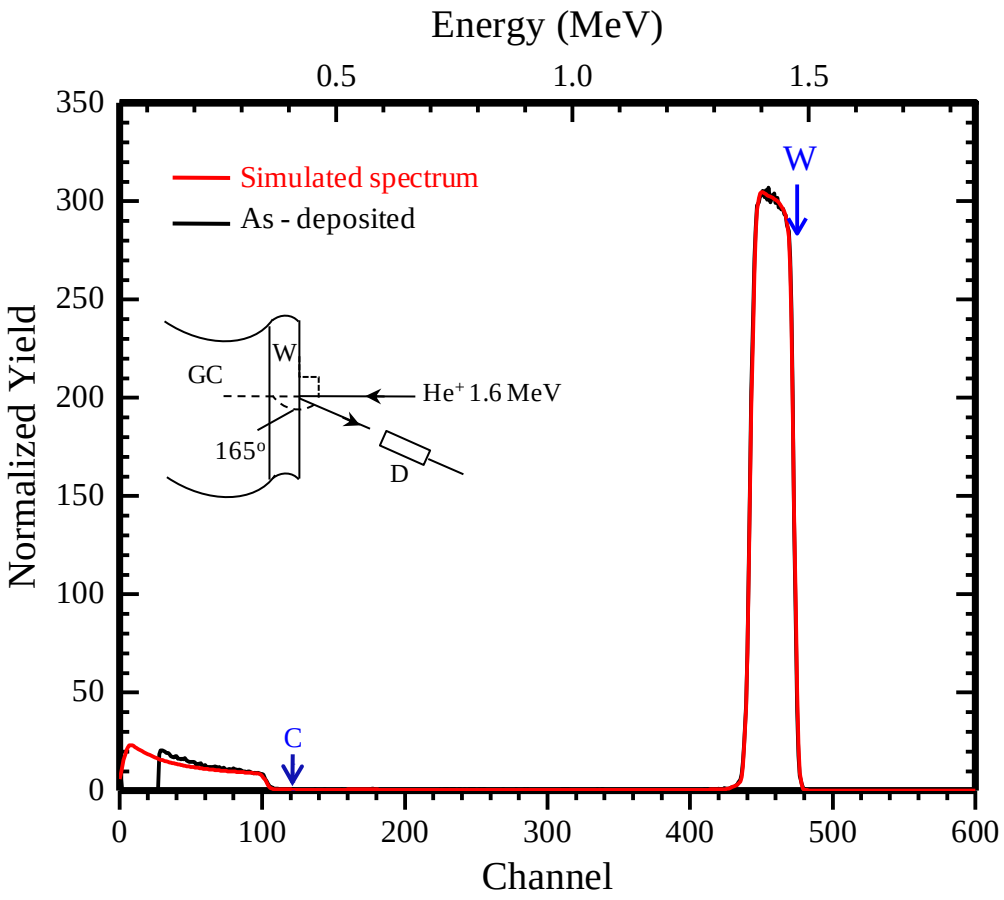

Fig. 1: RUMP simulated spectrum and RBS spectrum of as-deposited sample

RUMP simulations of RBS spectra were carried out after each annealing exercise to compare the inter-diffusion between W and glassy carbon. This was done by comparing the RBS spectra of samples annealed at 700, 800, 900 and 1000 ^{o}C with that of the as-deposited sample. Fig. 2 compares the RBS spectra of annealed samples with that of as-deposited sample to reveal the effect of heat treatment on the spectra of annealed samples. The overlay of spectrum of sample annealed at 600 ^{o}C on the spectrum of as-deposited sample showed that the two spectra overlapped almost perfectly on each other. This is an indication that annealing temperature of 600 ^{o}C was not high enough to induce diffusion at W-glassy carbon interface.

Comparison of spectrum of sample annealed at 700 ^{o}C with as-deposited spectrum showed that annealing at 700 ^{o}C, caused the back edge of the W peak to slightly shift towards lower energy channels. This is indicative of inter-diffusion setting in between W and glassy carbon atoms at this temperature. The simulated spectrum showed the formation of a small reaction zone (RZ) with a thickness of about 2 nm with composition of 8 at.% W and 92 at.% C. For the sample

annealed at 800 ^{o}C, the RBS spectrum showed a reduction in the W peak height and a further shift of the W back edge towards the lower energy channels. This shows further inter-diffusion and reactions taking place between W and glassy carbon with an increasing RZ estimated at 10 nm wide, but with the same atomic composition as that of 700 ^{o}C annealing.

For the sample annealed at 900 ^{o}C, the back edge of the W signal shifted further towards the lower energy channels with continued reduction in W peak height. A shift was also observed at the C high energy edge towards lower channels, with a step formed at the higher energy channels (inset in Fig. 2). The position of this step extends up to channel number 122 indicating that C had diffused substantially into the W film. This observation signifies further diffusion which led to formation of a wider reaction zone. The estimated RZ thickness after annealing at 900 °C was 14 nm with composition of 12.62 at.% W and 87.38 at.% C. It was observed that the W peak height further reduced in sample annealed at 1000 ^{o}C, with increased height of the step formed at the C high energy edge compared to that of 900 °C annealed sample. The average composition of the RZ was found to be 19.5 at.% W and 80.5 at.% C.

Generally, the intermixed region which formed after annealing at 700 °C got wider with increased annealing temperatures. The composition of the RZ which initially consisted of about 8 at.% W at 700 and 800 °C, increased to 12.62 at.% W and 19.5 at.% W at annealing temperatures of 900 and 1000 °C, respectively. This intermixing across the W and glassy carbon interface is governed by solid state reactions which could lead to formation of W carbides.

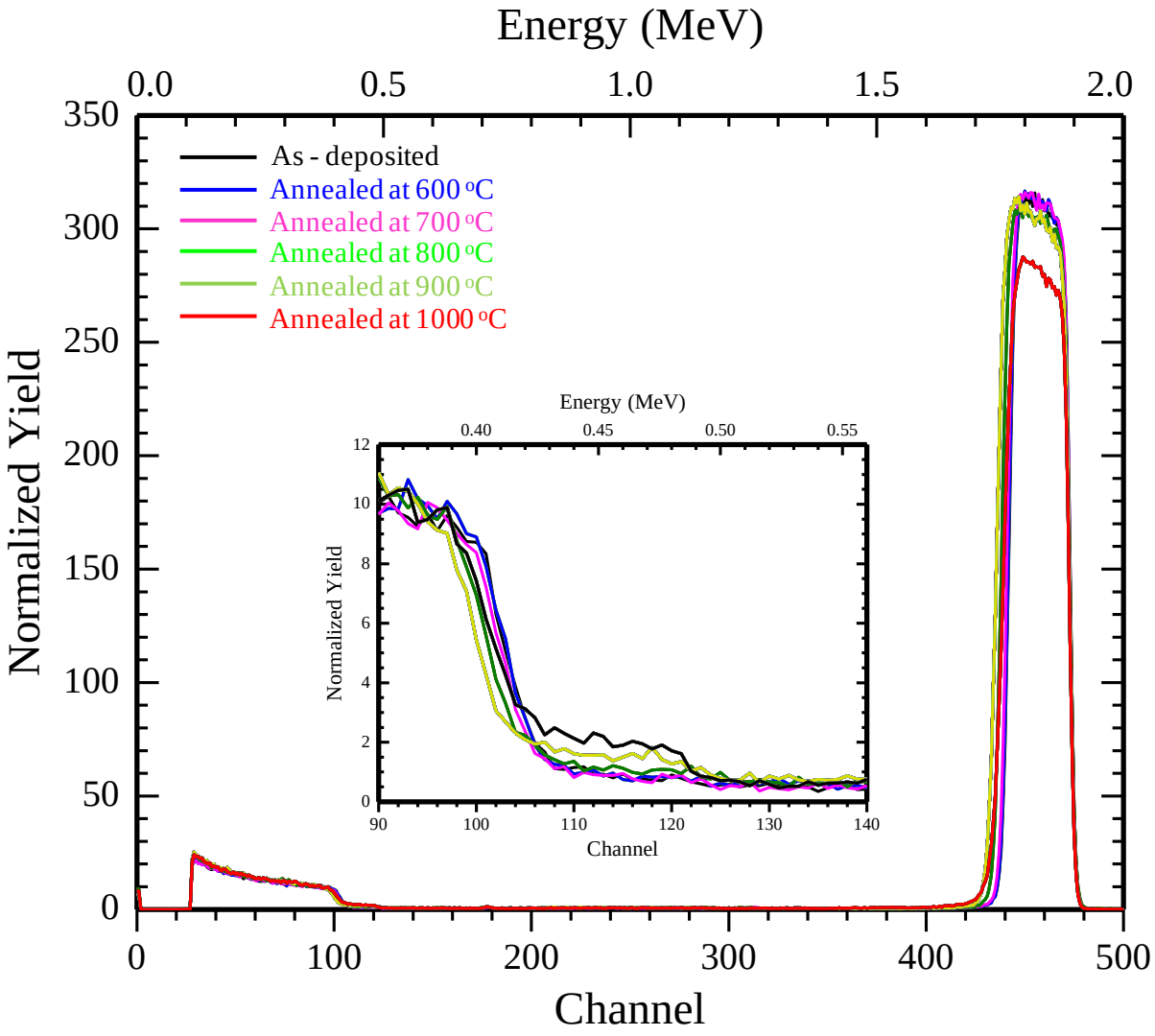

Fig. 2: Overlay of RBS spectra of W-glassy carbon annealed samples (600 - 1000 ^{o}C) on as-deposited sample. (Inset is a magnified glassy carbon edge for clarity).

The surface morphology of as-deposited and annealed samples was investigated by scanning electron microscope (SEM) analysis. Fig. 3 presents the SEM micrographs of the as-deposited W film surface and annealed samples surface. It can be observed from Fig. 3 (a) that the surface of as-deposited sample is smooth without any distinct feature indicating uniformity in W deposition. In Fig. 3 (b), the surface morphologies of samples annealed at 600 (and also at 700 ^{o}C but not shown here) are similar to that of as-deposited sample which is characterized by fairly

smooth surface. This implies that there is no change to the surface morphology as a result of heat treatment at these temperatures. In the SEM image of sample annealed at 800 ^{o}C Fig. 3 (c), the W film was no longer smooth but had small granular features on the surface which appeared after annealing at this temperature. Furthermore, the sample annealed at 900 °C (not shown here) had similar surface morphology with the one annealed at 800 °C. Fig. 3 (d) indicates that the surface morphology of the W-glassy carbon sample changed after annealing at 1000 ^{o}C. It can be seen that the surface roughness increased after annealing at this temperature compared to 800 °C which led to further change in surface morphology.

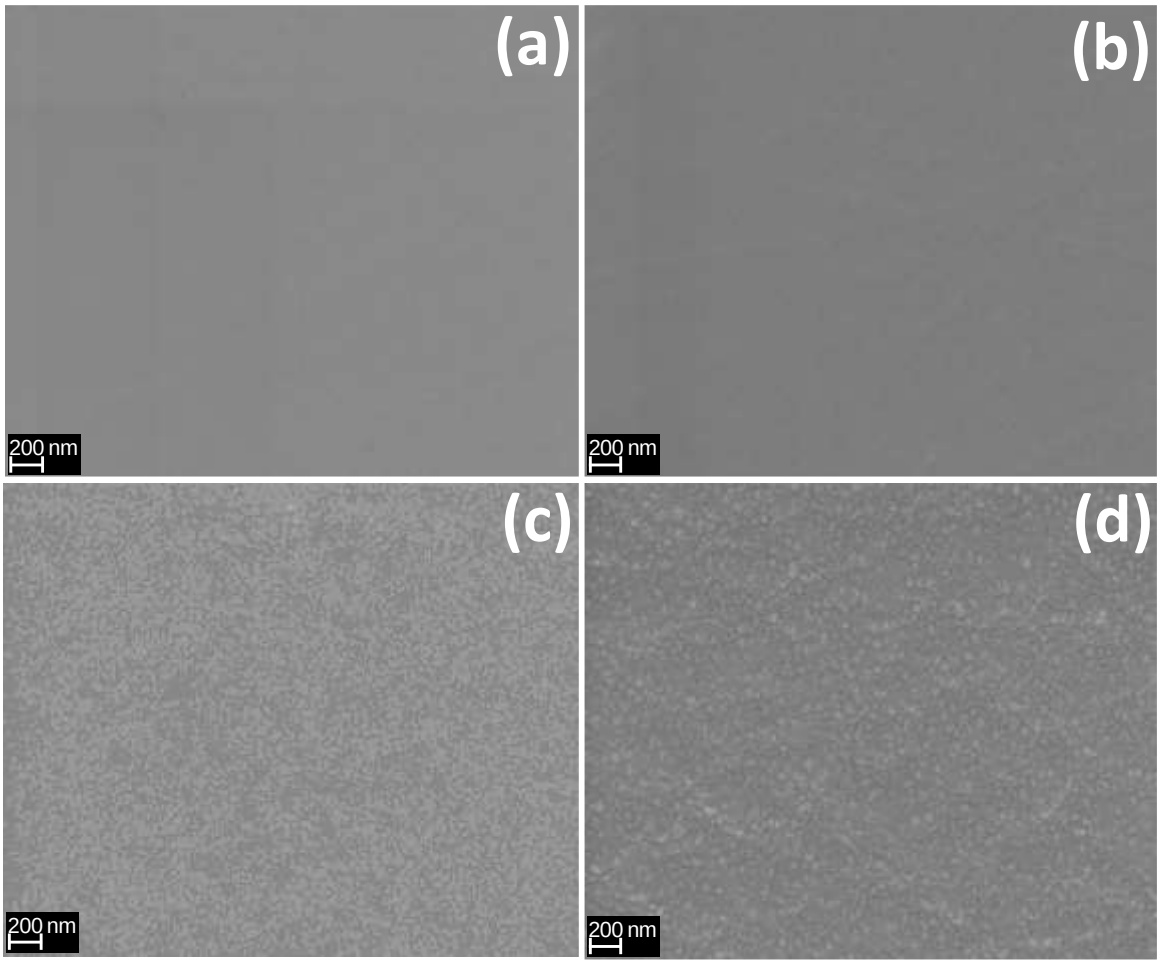

Fig. 3: SEM micrographs of W-glassy carbon samples (a) as-deposited; annealed at (b) 600 ^{o}C (c) 800 ^{o}C and (d) 1000 ^{o}C

4. Summary

The solid state interaction between W thin film and glassy carbon has been investigated using RBS and SEM analysis. It has been established by RBS-RUMP simulation that W and glassy carbon interact with each other strongly at annealing temperature of 700 ^{o}C and above. The surface of the as-deposited samples analysed with SEM showed uniform smooth W thin film layer, which decrease in the surface of sample annealed at 600 ^{o}C. SEM micrographs revealed that the surface roughness increased with temperature from 700 to 1000 °C. Two major properties required of nuclear waste containment material are effective corrosion resistance and radiation shield from the environment. It was observed that the W-glassy carbon is stable up to 700 °C, this suggests that the diffusion couple might improve the long-term structural integrity of dry cask storage devices for extended service lifespan.

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