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Deposition of CVD diamond onto Zirconium

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ABSTRACT

The growth of thin films of chemical vapour deposition (CVD) diamond onto flat samples of pure Zr has been studied using various CVD growth conditions in a hot filament reactor. We find that although growth is straightforward, adhesion of the diamond layer onto the Zr is poor, with the diamond layer often delaminating upon cooling. SIMS depth profiles show this to be due to the presence of a strongly-bonded native oxide on the Zr surface which is not removed in the reducing H_2 atmosphere during CVD. This, plus the lack of any substantial carbide interfacial layer to 'glue' the diamond onto the surface, together with a poor thermal expansion mismatch between Zr and diamond, and the Zr hcp-to-bcc phase transition at ~860°C, all lead to poor adhesion. Some of these difficulties can be reduced by depositing at lower temperature (<500°C) at the cost of poorer quality diamond.

INTRODUCTION

Zirconium alloys are used to make the hollow tubular fuel rods which hold the nuclear fuel in nuclear reactors. However at high temperatures it can react with the water coolant and corrode, releasing hydrogen as a by-product. Under exceptional circumstances (*e.g.* a meltdown event such as happened at Fukushima in Japan in 2011) enough hydrogen can be released that an explosion occurs, with potentially catastrophic results.

One possible solution to this is to coat the Zr with a layer of diamond to prevent the hot Zr coming into direct contact with water. Diamond is an ideal material for this because its high thermal conductivity will help transfer heat from the fuel-rods into the cooling water efficiently, while its low atomic number means that it will not absorb many neutrons and affect the nuclear reaction. Diamond is also mechanically robust and radiation hard. However, little has been reported yet about the growth of chemical vapour deposition (CVD) diamond onto Zr or Zr-alloys.

Zirconium is a Group IV second-row transition metal that is fairly soft and ductile, with a lustrous, pale grey appearance, and a melting point of 1855°C. Commercial Zr often contains ~1% hafnium which is difficult to separate due to their similar physical properties [1]. The properties of Zr, and in particular its high resistance to corrosion and very low neutron absorption, make it an ideal candidate for certain applications within the nuclear industry. Most uses are structural, and it has been used as such and as fuel cladding since the 1950s. In nuclear reactors, Zr is not used as the pure metal, but instead made into one of several alloys, mainly to further increase its hardness and corrosion resistance. Two of the most common alloys go by the names of Zircaloy-2 and Zircaloy-4, and contain small amounts of Sn, Fe, Ni, Cr and O, with Hf content <0.1%.

In order to form an adherent diamond film on a substrate, normally the substrate material must form a thin carbide layer at the interface which acts to glue the diamond in place. Zr does form a stable carbide, however, high temperatures of ~2000°C are required to synthesise ZrC from Zr and carbon, which is usually carried out by sintering at 40 MPa pressure [2], or carbothermic reduction of Zr in a graphite furnace at [3,4]. Unfortunately, substrate temperatures in a hot filament or microwave CVD diamond reactor usually do not exceed 1000°C, which means direct carbide formation from hydrocarbon gas species might be problematic. One previous study [5] using Zr in an arc discharge plasma CVD system showed that both ZrC and ZrH can be formed at the diamond-Zr interface, so long as high enough substrate temperatures (900-1000°C) are employed. Another potential problem is that the surface of zirconium will react with any oxygen present in the surrounding atmosphere to form a passivation layer between 2-5 nm thick [6] of zirconium oxide, ZrO_2, an extremely stable material that will not decompose except under very harsh conditions. It is because of this protective surface oxide that Zr is so resistant to heat and corrosion, allowing for its use in nuclear power as well as harsh chemical environments. For some materials, such as Si, the presence of a native oxide does not impede diamond CVD, because the H_2 atmosphere can reduce most or all of the oxide before diamond growth begins. Thicker, stable oxide materials, such as quartz (SiO_2), sapphire (Al_2O_3), or titania (TiO_2), however, are often problematic substrates for diamond CVD. This is probably due to the tendency of the adsorbing carbon radicals to bond with the surface oxygens, resulting in volatile CO and CO_2. This leads to etching rather than film growth, or if a film grows, to a poorly adherent interface. ZrO_2 is so stable that it will not be displaced by hydrogen in favour of creating the hydride. Instead, heating it to over 500°C in vacuum causes the oxygen to diffuse away from the surface into the bulk metal allowing the hydride to be formed [3]. Deposition at high temperatures brings the additional problem of a mismatch in coefficients of thermal expansion. If diamond is to grow on a zirconium substrate it is desirable that the extent to which each expands under heating is as close as possible. Diamond expands very little when heated (just 1 $\mu m\ m^{-1}\ K^{-1}$), and at 5.7 times larger, the expansion coefficient of zirconium is considerably more, which may pose a risk of the diamond film delaminating from the substrate upon cooling down from the deposition temperature. However, by comparison, successful diamond growth is frequently observed on molybdenum substrates, which have a thermal expansion coefficient of 4.8 $\mu m\ m^{-1}\ K^{-1}$ [26], which suggests that the diamond is able to sustain a certain amount of stress provided a strong enough carbide interface is formed. Unfortunately, there is a further problem with Zr, in that it undergoes a phase transition from hcp to bcc at ~860°C [7], with a corresponding 66% decrease in volume. The transition temperature is very close to that used for diamond CVD, and if this temperature is exceeded, upon cooling after deposition the bcc Zr substrate will revert back to the low-temperature hcp form with its higher volume, placing great strain upon any rigid diamond layer growing on it.

In this paper we examine the growth of CVD diamond onto Zr substrates using a standard hot filament reactor, and investigate the adherence and interface properties as a function of deposition conditions.

EXPERIMENTAL

Zirconium (99.2% purity) was purchased from Goodfellows (ZR000290) as a sheet 0.2 mm thick, and then laser cut into flat samples 1 cm^2 in size. Before deposition the Zr substrates were manually abraded using 1-3 µm diamond powder. CVD was performed using a hot filament reactor utilising standard deposition conditions that are known to deposit microcrystalline diamond at a rate of ~0.5 µm h^{-1} on other (diamond, Si or Mo) substrates [8]. Briefly, a gas mixture of 1%CH_4/H_2 at 20 torr is used, with the substrate being heated radiatively from a Re filament situated 5 mm above the substrate surface. For standard conditions, the filament temperature was 2400 K which resulted in a substrate temperature T_s~1173 K. The substrate temperature was reduced by reducing the filament temperature. However, this also affected other growth parameters such as the H atom concentration, growth rate, crystal size, *etc*. Three experiments were performed at different substrate temperatures, T_s~1173 K, ~1023 K, and ~873 K.

Films were analysed with laser Raman spectroscopy (Renishaw 2000) using green (514 nm) excitation to determine film quality and crystallinity. Secondary ion mass spectrometry (SIMS) depth profiling was performed using an in-house built magnetic sector-secondary ion mass spectrometer (MS-SIMS) with a gallium ion gun [9]. Separate scans were done to detect both positive and negative secondary ions. The majority of ions detected were positive, as would be expected from a metallic substance. However, scanning for negative ions was used to obtain a clearer signal from the non-metallic compounds present, such as oxygen, ZrO_x and carbon.

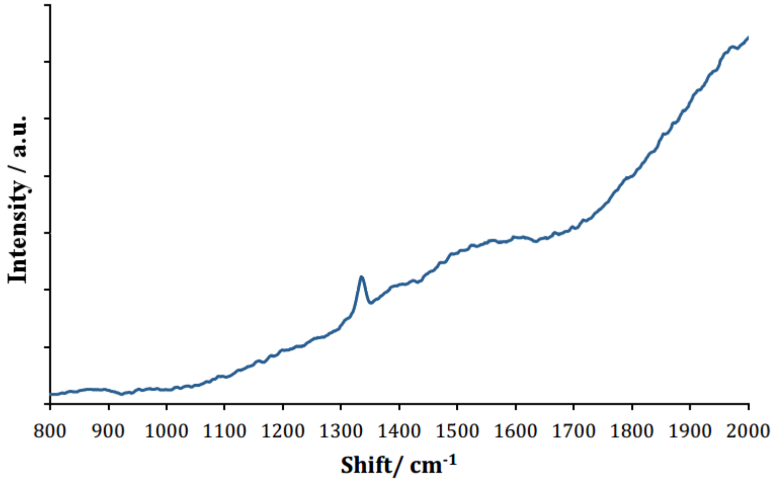

Figure 1. Raman spectrum of the microcrystalline diamond film grown on Zr at 873 K, showing the diamond peak at 1332 cm^{-1} along with the G-band at 1550 cm^{-1} and rising background due to scattering from grain boundaries.

RESULTS

Growth at 1173 K for 8 h resulted in the formation of a uniform layer of CVD diamond about 4 µm thick. However, upon cooling, the film cracked into flakes and completely delaminated. Either the adhesion of the film onto the Zr surface was poor, or the thermal expansion mismatch too great, or both. Growth at 1023 K for 6 h resulted in isolated crystals of diamond on the surface, due to the lower temperature decreasing the growth rate. Increasing the deposition time to 12 h resulted in a continuous diamond film, but this was followed by cracking, flaking and delamination, as before. Growth at 873 K required 30 h, as the deposition rate at this temperature had slowed to ~0.03-4 µm h^{-1}. Raman spectra (Fig.1) and scanning electron micrographs (SEM) (Fig.2) show that the film is diamond, but the quality of the film is poor, with some graphitic sp^2 carbon present, as expected from the low deposition temperature.

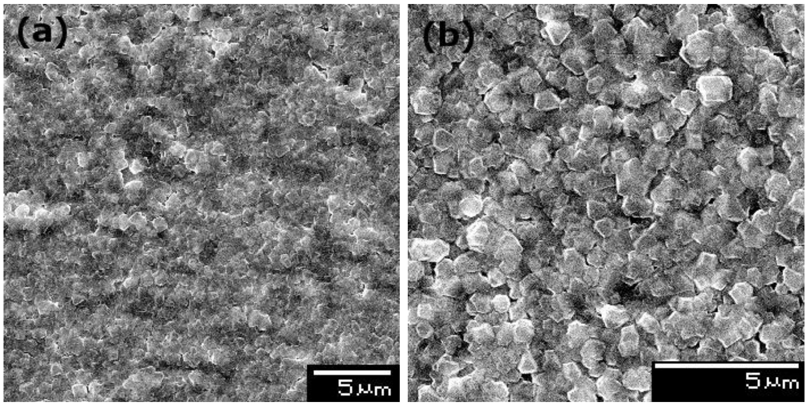

Figure 2. SEM images of the diamond film grown on Zr at 873 K, at low (a) and high (b) magnification. The film is microcrystalline and facetted, and although continuous it contains a few pinholes revealing the Zr substrate beneath. The film is approximately as thick as a single crystallite, estimated to be ~0.75 µm.

Figure 3 shows the positive and negative SIMS depth profiles for the diamond film grown at 873 K. The absolute depth was estimated based on the etch time. The Zr etch rate was estimated to be 0.29 nm s^{-1} using the computer package *SRIM* [10], while that for diamond was 0.6 nm s^{-1} based upon a calibration performed with a pure diamond sample. Averaging these, we used 0.45 nm s^{-1} as the mean etch rate for the composite material, although we acknowledge that this approximation will underestimate the thickness of the diamond layer and overestimate the thickness of the Zr. The absolute concentrations of each species cannot be determined without calibration sample for the SIMS intensities, which were not available. Therefore, the signals from each species have been plotted on an arbitrary scale, with the maximum signal value (full scale deflection) for each species given in the caption, so that the reader can judge the relative magnitudes of the signals. Both (a) positive and (b) negative SIMS spectra are consistent. The signal from C from the diamond decays around 0.75 µm, which is consistent with the film thickness estimated from SEM in Fig.2. The Zr peak maximizes at a depth of ~1 µm, which suggests that there is 0.25 µm of mixed material between the diamond and Zr. This could simply be an artefact of SIMS depth profiling (i.e. SIMS mixing), or an uncertainty in depth due to the surface roughness. However, it could also indicate a true bonding of Zr and C to form a zirconium carbide. Interestingly, the peak from C_2^+ in Fig.3(a) shows that this species is concentrated around the diamond-Zr interface, possibly indicating a carbide layer. Hf is present at about 1% that of the Zr signal, as expected. The most important peaks are those for O^+ and O^-, which peak slightly to the metal side of the diamond-Zr interface. This shows that the robust oxide layer on the Zr metal was not reduced away during the low temperature CVD process, and is still present at or near the interface.

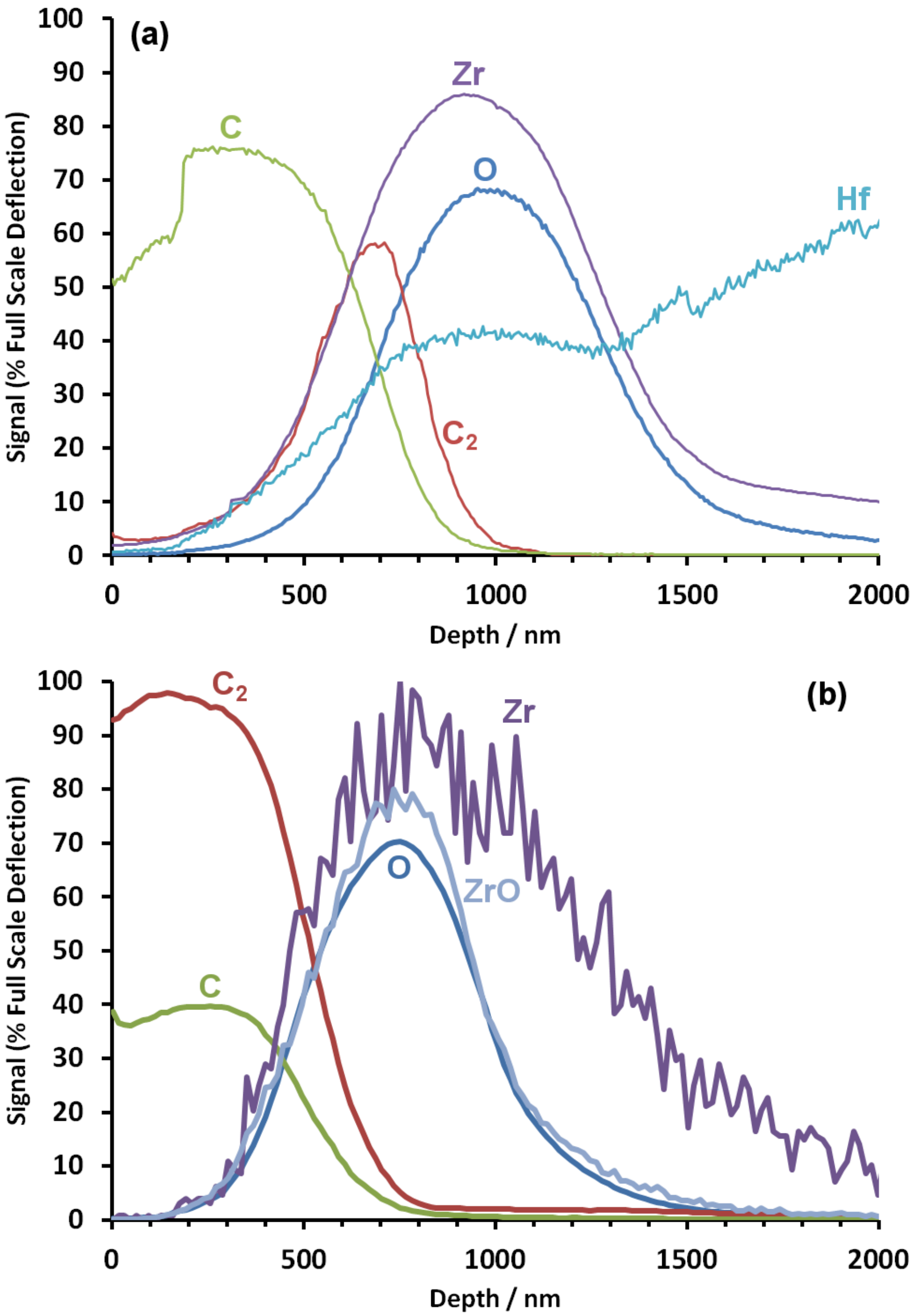

Figure 3. SIMS depth profiles of the diamond film on Zr grown at 873 K. (a) Detecting positive ions, with the signal being shown as a percentage of the full-scale deflection (f.s.d.) for each species. The values for f.s.d. were: C^+ 50000, Zr^+ 1.1×10^6, O^+ 67000, C_2^+ 193000, and Hf^+ 8000. (b) Detecting negative ions, with the signal for the metals now being much smaller, and that for Hf^- below the instrument background sensitivity. The f.s.d. values were: C^- 111000, C_2^- 325000, O^- 1.3×10^6, Zr^- 130, ZrO^- 3400.

CONCLUSIONS

The results show that depositing an adherent CVD diamond layer on Zr is not straightforward. The Zr phase transition at 860°C and corresponding volume change mean that at deposition temperatures above this value, which are desirable for high growth rate and high quality diamond, the diamond film is put under such compressive stress during cooling that it cracks and flakes off. Reducing deposition temperatures to 700°C helps with this problem, but the large expansion mismatch between the two materials means poor adhesion still results. Although there is some evidence for a small amount of carbide formation at the interface (consistent with the findings of ref.[5]), there is not sufficient present to stick the film to the substrate strongly enough to overcome the stress. This lack of adhesion leads to film delamination. At lower deposition temperatures the expansion mismatch problem is reduced, however there is now insufficient energy to reduce the native Zr oxide, which remains at or near the interface, further preventing film adhesion. Continuous coatings can be deposited at these low temperatures (<600°C), but the diamond quality is poor and the film thin and full of pinholes. One possible solution to this may be to remove (chemically or otherwise) the oxide layer prior to diamond CVD, although this would likely be a non-trivial procedure due to the stability of ZrO_2. Furthermore, the affinity of Zr for oxygen means that upon exposure to air the clean Zr surface would immediately reoxidise. Care would need to be taken to ensure the clean Zr was kept under an inert atmosphere while loading it into the CVD chamber - again not trivial. A suggestion may be to sputter off the oxide layer using an Ar plasma in a microwave CVD reactor, and then without breaking vacuum, perform the diamond deposition step. Another possible solution to the adhesion problem may be to etch microstructured ridges into the Zr to mechanically ‘lock in’ the diamond layer. Another may be to use a diamond growth process which can deposit at even lower temperatures, *e.g.* 400°C, such as a linear antenna microwave system. Indeed, recent results from the Czech Academy of Sciences [11] combining these two ideas show that low-temperature deposition of continuous diamond films on Zr-alloy cylinders is feasible. However, the growth rates in their linear antenna system are very low and the film adherence strength was not reported. Nevertheless, with use of a suitable barrier layer to improve adhesion this problem may be solved.

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