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Research on thermal stability of DLC by using in-situ Environmental Scanning Electron Microscope

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ABSTRACT – It is necessary to attach importance to the thermal stability of DLC, when it is applied as a protecting coating in high temperature environment. It has been reported that ta-C coating shows excellent thermal stability among the DLCs, and it can endure the temperature up to 400ºC in air. However, the mechanism of its deterioration was not investigated clearly. This paper focuses on the in situ observation on ta-C coating in heating process, as well as the effect of gas environments. The in situ observation was conducted by Environmental Scanning Electron Microscope (ESEM) with heating stage in air, N_2 and O_2. It revealed that the existence of oxygen is an important factor leading to the deterioration of ta-C. Besides, the cross-section observation shows that there two kinds of defects in the coating. These two kinds of defects show different oxidation phenomenon.

1. INTRODUCTION

Diamond-like carbon (DLC) has found widespread application in many fields. In some of these applications, the coatings are subject to high temperatures environment. The thermal stability and the tribological properties of a-C:H coatings have been reported [1], it was revealed that hydrogen released from the coatings when it was heated up to 300 ºC. Tetrahedral amorphous carbon (ta-C) coating, a kind of hydrogen free DLC, is considered to show better thermal stability. In our precious research [2], the high temperature tribological properties of ta-C have been investigated. Moreover, the oxidation resistance was also discussed. It was found that many white points (1~10μm) can be observed by SEM on oxidized surface. However, the formation of these points and the mechanism of ta-C deterioration are not clear. In this paper, ESEM was used to in situ observe the oxidation process. Besides, the effects of different gas environment on oxidation rate were discussed.

2. EXPERIMENTAL METHOD

The ta-C coating with thickness of 0.7 μm and hardness of 45 GPa was prepared by Filter Cathode Vacuum Arcing (FCVA) method. A chromium interlayer was prepared in order to improve the adhesion force of ta-C coatings.

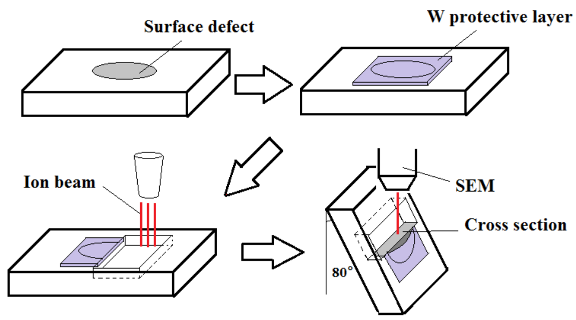

Figure 1 Schematic of ESEM observation on cross section of surface defect.

The thermal stability of ta-C was evaluated by ESEM with a heating stage. The heating test was conducted at 650ºC in N_2, air and O_2 atmosphere, and the pressure of ESEM chamber was set as 130Pa. The deterioration rate of the ta-C, can be observed by ESEM. Deterioration area was calculated based on the binaryzation of SEM photos. The structure transformation of ta-C was detected by Raman spectroscopy. The cross-sections of the defects, which were manufactured by focused ion beam (FIB) cutting, then observed by FE-SEM, as shown in Figure 1. The element distribution in section was detected by using Energy Dispersive x-ray Spectroscopy (EDS).

3. RESULTS AND DISCUSSION

Figure 2 shows the deterioration ratio of ta-C in O_2, air, N_2 atmosphere. In N_2, the coating did not change a lot; in air and O_2, the deterioration areas show exponential growth, and deterioration rate in O_2 is much higher than that in air.

Figure 3 shows the two types of defects and their changes in heating process. Some small white points (red circles in Figure 2) were becoming larger in heating, named as type 1. Another kind of black point, a little bit bigger than type 1 (yellow circles in Figure 2), turned white in heating process, named as type 2.

It is assumed that two reasons leading to color change in SEM, structure transformation and topography change. Firstly, Raman spectroscopy was used to measure the structure of the defects. Figure 4 shows the Raman spectroscopy of ta-C at different area. The D peak of type 1 increased slightly after heating. The peaks of type 1 look almost same as the normal area. For the type 2, the D peak increased greatly. It means graphitization is the main reason of deterioration on type 2 rather than type 1.

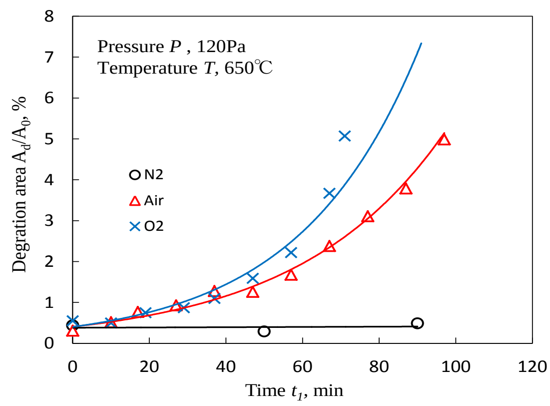

Figure 2 Deterioration area ratio of ta-C coating heated in O_2, air, N_2 atmosphere.

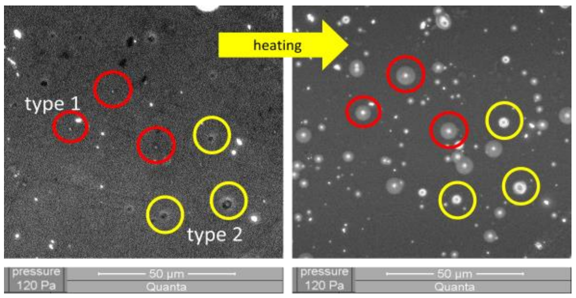

Figure 3 ESEM of ta-C before and after heating in O_2.

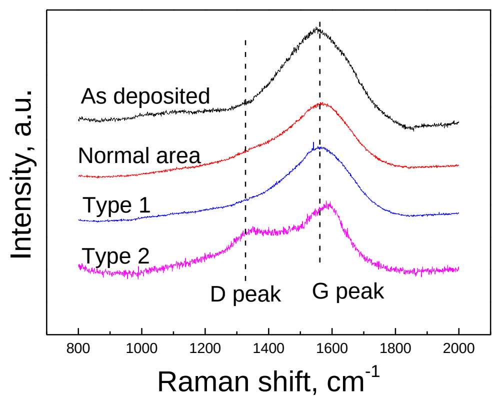

Figure 4 Raman spectroscopy of ta-C at different area.

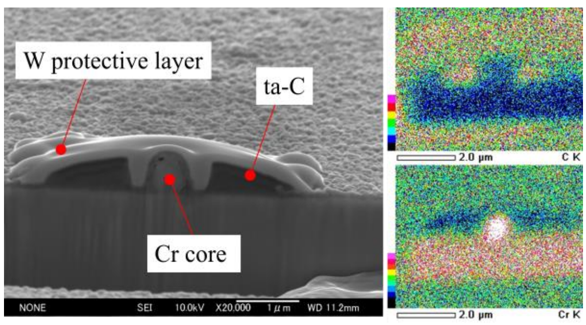

Figure 5 SEM and EDS mapping of type 1 defect after heating in oxygen.

In order to confirm the topography change, both two types of defects were cut by FIB, and the cross-sections were observed by FE-SEM. Figure 5 and 6 show the cross-section images of defect type 1 and 2 respectively. For type 1, there is a chromium core in the center of defect. The ta-C coating became a dome around it. For type 2, there is almost no carbon remained on the defect area, since only protective layer (tungsten) was detected by EDS.

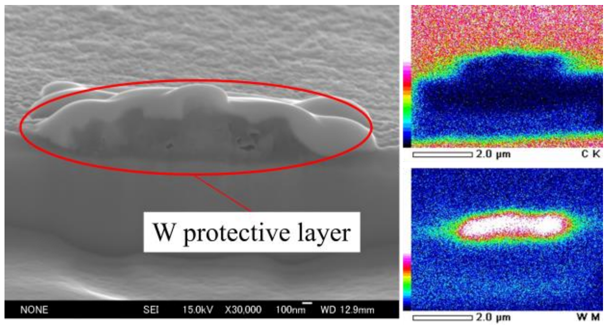

Figure 6 SEM and EDS mapping of Type 2 defect after heating in oxygen.

In the process of FCVA ta-C deposition, the droplets were difficult to be filtered completely. Therefore, some droplets with low density exist in Chromium interlayer and ta-C coating. When the coating containing chromium droplet was heated, oxygen got into the coating through the small holes, which can be seen in the SEM image. Then the interface was oxidized, adhesion force became weak and ta-C around chromium droplet was the first to peel off. This phenomenon caused the formation of type 1. On the other hand, carbon droplets show lower sp^3 structure, which is less stable than normal coating. [3] When ta-C coating with carbon droplet was heated, coating around the carbon droplet oxidized to CO or CO_2. This is the mechanism caused the formation of type 2.

4. CONCLUSIONS

This research revealed that deterioration rate of ta-C is the highest in O_2. Two types of defects, type1-Chromium droplets and type 2-carbon droplets were discussed. In heating process, type 1 shows interface oxidation and peeling off mechanism; type 2 shows carbon chemical reaction and disappearing mechanism.

5. REFERENCES

[1] X. Deng, K. Hiroyuki, T. Tokoroyama and N. Umehara. Thermal stability and high temperature tribological properties of a-C:H and Si-DLC deposited by microwave sheath voltage combination plasma. Tribology Online, 8(2013) pp. 257-264.

[2] X. Deng, K. Hiroyuki, T. Tokoroyama and N. Umehara. Tribological behaviors of tetrahedral amorphous carbon (ta-C) coatings at elevated temperature. Tribol. Intl., 75(2014), pp. 98-103.

[3] R. Kalish, Y. Lifshitz, K. Nugent and S. Prawer. Thermal stability and relaxation in diamond-like-carbon. A Raman study of films with different sp3 fractions (ta-C to a-C) Appl. Phys. Lett. 74 (1999), pp. 2936-293.