Stress and adhesion of B₄C films for boron–coated neutron detectors

Feng Qin xu, Qi Run ze, Li Wen bin, Ni Hang jian, Huang Qi shi, Zhang Zhong, Wang Zhanshan

(MOE Key Laboratory of Advanced Micro–structured Materials, Institute of Precision Optical Engineering, School of Physics Science and Engineering, Tongji University, Shanghai 200092, China)

Abstract: As an alternative to ³He neutron detectors, boron–coated neutron detectors have been a current focus for researchers worldwide. For the boron–coated neutron detectors, a B₄C film with low stress and good adhesion to the Al substrate is required. To enhance adhesion of the B₄C films on Al substrates, a B₄C film with low stress was fabricated by direct current sputtering technique without substrate–heating. The Mg–Al alloy thin film was introduced between the B₄C film and its substrate for enhancing the adhesion. The effect of sputtering pressure on the stress of B₄C films during deposition was studied. Additionally, the adhesion of B₄C films using Mg–Al films as adhesive layers and effects of sputtering pressure and alloy film thickness on adhesion were studied. Scanning and transmission electron microscopies were used to characterize the microstructure. Experimental results show that the stress of B₄C films decreases and stabilizes when sputtering pressure increases during deposition. Thin and porous Mg–Al films react well with both B₄C films and Al₂O₃ on Al substrates to enhance adhesion of the B₄C films, without substrate–heating.

Key words: boron–coated neutron detector; stress; Mg–Al alloy film; adhesion

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0 Introduction

As an alternative to \(^{3}\text{He}\) neutron detectors, boron–coated neutron detectors, such as multi-gap resistive plate chamber, boron–coated ion chamber, and boron–coated straw detector, have become a research hotspot worldwide\(^{11}\). Generally, the neutron detector based on \(^{3}\text{He}\) is the main equipment used for neutron detection. However, the limited supply and extensive consumption of \(^{3}\text{He}\) gas has made it necessary to develop a new technology for the growing demands of neutron detection. As 10 B has a high thermal cross section, high detection efficiency and low \(\gamma\) cross section, the boron–coated detector is used as an alternative for neutron detection\(^{2}\).

To manufacture the boron–coated detector, a thick B\(_{4}\)C film is required to be coated on a metal substrate such as Al and Cu\(^{3–4}\). To meet the need of the neutron spectrometer of CSNS (China Spallation Neutron Source), a B\(_{4}\)C film of thickness 1.2 \(\mu\)m was selected to be coated in this research\(^{3}\). In this paper, a commercially available Al sheet was selected as the substrate because of its good thermal and electrical conductivity, less absorption of neutrons, and low density \(^{4}\). However, the complications with a commercial Al sheet include the unavoidable layer of aluminum oxide and considerable roughness on the surface. Thus, the adhesion of a thick B\(_{4}\)C film on Al substrate is very poor. B\(_{4}\)C film with good adhesion was deposited with substrate–heating in the study of Hoglund C. However, high temperature can deform the aluminum substrates and thin films \(^{7–8}\). In this paper, the direct current sputtering technique of B\(_{4}\)C film with good adhesion without substrate–heating is studied. In this technique, a thick B\(_{4}\)C film with low stress is required to prevent peeling off\(^{9}\). Additionally, the adhesive layer between the B\(_{4}\)C film and Al substrate was introduced \(^{10}\). In order to enhance the adhesion, a remarkable reaction or a huge diffusion at the interface between the adhesive layer and lower oxide layer, and at the interface between the adhesive layer and upper B\(_{4}\)C layer is essential. As reported in previous studies, a few active metals, such as Ti and Mg, can react with both Al\(_{2}\)O\(_{3}\) and B\(_{4}\)C\(^{11}\). In this paper, the Mg–Al alloy film was selected as the adhesive layer for the better adhesion between B\(_{4}\)C film and Al substrate than Ti or Mg.

This paper focuses on the study of the stress and adhesion of B\(_{4}\)C films. Using the results of scanning electron microscopy (SEM) and transmission electron microscopy (TEM), the microstructures and the reaction at the interfaces are investigated. The effects of different parameters during the deposition process are discussed, including the thickness of the Mg–Al alloy film and the sputtering pressure during the deposition of the B\(_{4}\)C film and the Mg–Al alloy film. An appropriate method is proposed to coat a 1.2 \(\mu\)m thick B\(_{4}\)C film on a commercial Al substrate for the boron–coated detector.

1 Experiments

In this research, the Mg–Al alloy film and the B\(_{4}\)C film were deposited on the commercial aluminum substrates (Model: AA 1060) of dimension 10 mm \(\times\) 20 mm and thickness 0.3 mm using the direct–current (DC) magnetron sputtering deposition method. The base pressure inside the
chamber before deposition was better than $3\times10^{-4}$ Pa. During the deposition process, high purity argon (99.999\%) was used as the sputtering gas. The sputtering rates of Mg–Al alloy and B$_3$C were 5.733 $\text{Å}/\text{s}$ and 1.0953 $\text{Å}/\text{s}$, respectively.

Before deposition, aluminum substrates were processed using the chemical mechanical polishing process to minimize the roughness. Then the substrates were cleaned using a water–based detergent to remove oil and other contaminants, cleaned using water next, and naturally dried at room temperature. After the deposition of the Mg–Al alloy film and the B$_3$C film, the grazing incident X–ray reflection (GIXR) measurements were carried out using an X–ray diffractometer equipped with Cu K$\alpha$ line ($\lambda = 0.154$ nm). By fitting the GIXR curves using the Bede REFS software (genetic algorithm), the thicknesses of the Mg–Al alloy film and the B$_3$C layer were determined\textsuperscript{125}. The stress measurements were carried out on the B$_3$C films developed on polished quartz substrates of diameter 20 mm and thickness 1 mm. The laser interferometer was used to measure the radius of curvature of quartz substrates before and after coating, and the multilayer stress was determined using the following modified Stoney equation:

$$\sigma_f = \frac{1}{R_{\text{post}}-1/R_{\text{pre}}} \left( \frac{E_s}{(1-V_s)} \right) t_f^2 / 6 t_f$$  \hspace{1cm} (1)

where $t_s$ is the substrate thickness, $t_f$ is the film thickness, and $R_{\text{pre}}$ and $R_{\text{post}}$ are the radii of curvature of the sample before and after deposition, respectively. $E_s$ is Young’s modulus and $V_s$ is the Poisson’s ratio of the substrate. Tape bonding experiments were performed to evaluate the adhesion of the B$_3$C film on Al substrate qualitatively\textsuperscript{126}. SEM was conducted for microscopic detection for the results of the tape bonding experiments. The test was supported by the Materials Analysis Technology Inc. (MA–tek) and realized using FEI 201. The microstructures of the deposited samples were analyzed by TEM using the FEI G2F20 Tecnai instrument provided by Materials Analysis Technology Inc. (MA–tek).

2 Results and discussion

2.1 Stress measurements

Several methods, such as annealing, and heating up the substrate and increasing the sputtering pressure, are used to reduce the intrinsic stress of the deposited films. For B$_3$C films, the effect of the sputtering gas pressure on the film stress was studied. The B$_3$C films of thickness 100 nm deposited on quartz substrates without adhesive layers were fabricated at four different sputtering pressures of 0.53, 0.67, 0.93, and 1.20 Pa. The measured stress of B$_3$C films is shown in Fig.1. The compressive stress of the B$_3$C film deposited at the sputtering pressure of 0.53 Pa is $-1\,090.25$ MPa, which is considerably large. The stress decreases to $-375.44$ MPa when the sputtering pressure increases to 1.20 Pa. Finally, it is observed that the stress tends to stabilize as the sputtering pressure increases.

![Fig.1 Stress results of B$_3$C films deposited at four different sputtering pressures of 0.53, 0.67, 0.93, and 1.20 Pa](image)

The B$_3$C film usually becomes porous at a high sputtering pressure due to the decrease in the mean free path of gas molecules \textsuperscript{114}. This porous structure leads to more defects in the B$_3$C film. Due to the effect of surface tension, the compressive stress will decrease. By optimizing
the sputtering gas pressure, the compressive stress can be minimized. Thus, the higher the sputtering pressure during the B,C film deposition, the lower the stress of the B,C film is.

2.2 Adhesion experiments

To enhance the adhesion of the B,C film on Al substrate without substrate-heating, a Mg–Al alloy film was inserted between them. The effects of sputtering pressure and alloy film thickness on adhesion were studied here. For optimizing the adhesive strength, six samples were fabricated under different conditions. The Mg–Al alloy films in Samples 1, 2, 3, and 4 were deposited on Al substrate at the pressure of 1.33 Pa with thicknesses of 0, 15, 100, and 400 nm. The Mg–Al alloy films in Sample 5 and 6 were deposited on Al substrate at the pressure of 0.13 Pa with thicknesses of 15 and 100 nm. Each B,C film in these six samples was deposited on Al substrate at the pressure of 1.33 Pa with the same thickness of 1.2 μm.

The pictures of six samples after coating are shown in Fig.2. It can be observed that thin films peel off completely in Samples 1, 4, and 6, and a few parts of the film peel off near the edges in Sample 3. However, thin films adhered well to Al substrates in Samples 2 and 5.

To compare the adhesive strengths of Samples 2 and 5, the tape bonding experiment was carried out. The tape used in this experiment was Scotch 600 transparent tape manufactured by the 3M company. The peel adhesion of this tape was 3.0 N/cm. In this test, Samples 2 and 5 were taped five times. The pictures and micrographs of Samples 2 and 5 before and after bonding are shown in Fig.3.

In Fig.3, Sample 2 shows very small changes after bonding. However, a small white dot appears on Sample 5 after bonding, as shown by the red circle in Fig.3(d).

The cause of the white spot in Sample 5 was further studied using SEM. Firstly, the area of the white spot was cut using a focused ion beam (FIB) to expose the cross section. Next, the cross section was observed by SEM, which is shown in Fig.4. It can be seen that the upper three layers, including the Pt layer, the W layer, and the SiO₂ layer, are protective layers of FIB, which increase the etching rate. Only Al substrate is present underneath the protective layers. The absence of the Mg–Al alloy film and the B,C film indicates...
that the appearance of the white spot was due to the disconnection of the Mg–Al alloy film from Al₂O₃.

From the above results, the following conclusions can be drawn. Firstly, by comparing Sample 1 to Sample 2, the Mg–Al alloy film between Al substrate and B₄C film can effectively enhance the adhesion of B₄C films. Secondly, the thickness of the Mg–Al alloy film should not be too thick. In this paper, the best adhesion of B₄C films was obtained when the thickness of the Mg–Al alloy film was 15 nm, and the adhesion apparently became worse as the thickness increased. Finally, by comparing Sample 3 to Sample 6, and by analyzing the results of tape bonding experiments, it was observed that the sputtering pressure during the Mg–Al alloy film deposition also had an important effect on the adhesion of B₄C films. The higher the sputtering pressure, the stronger the adhesion of B₄C films is. Thus, a relatively thin Mg–Al alloy film deposited at a high sputtering pressure can increase the adhesion of a B₄C film on Al substrate without substrate-heating.

2.3 Transmission electron microscopy

To further study the internal microstructure of B₄C films, TEM was performed on Samples 2 and 5. The bright-field cross-sectional TEM micrographs of two samples are shown in Fig.5. In Fig.5(a) of Sample 2, each layer from top to down is the B₄C film, the diffusion layer between the Mg–Al alloy film and B₄C film, the mixture of the Mg–Al alloy film and Al₂O₃, the diffusion layer between the Mg–Al alloy film and Al substrate, and Al substrate. The Mg–Al alloy film diffused well with both upper and lower layers. Reaction between the Mg–Al alloy film and Al₂O₃ was strong. In Fig.5 (b) of Sample 5, each layer from top to down is the B₄C film, the Mg–Al alloy film, Al₂O₃, and Al substrate. There is a clear interface between each layer. Diffusion between the Mg–Al alloy film and B₄C film was weak. A clear stratification between the Mg–Al alloy film and Al₂O₃ clearly illustrated that there was a small amount of diffusion between them.

![Fig.5 Bright-field cross-sectional TEM micrographs of (a) Sample 2 and (b) Sample 5](image)

A conclusion can be drawn that the sputtering pressure during the Mg–Al alloy film deposition played an important role in the microstructural changes. If the sputtering pressure during the Mg–Al alloy film deposition is higher, the mean free path of metal atoms is shorter, and the probability of collision with Ar atoms/ions is higher. If the energy of metal atoms impacting the substrate is lower, the Mg–Al alloy film is porous. Sample 2 deposited at a high sputtering pressure had a porous Mg–Al alloy film, whereas Sample 5 deposited at a low sputtering pressure had a more compact Mg–Al alloy film.
Usually, a porous layer has a large void ratio. According to Fick’s first law\cite{15}, the diffusion coefficient increases with the increase in the void ratio, hence, a porous Mg-Al alloy film can diffuse better with other layers. This is the case for Sample 2, and hence, the deposited Mg-Al alloy film diffused well with both B,C film and Al₂O₃. The Mg-Al alloy film for Sample 5 was compact, and hence, it had a weak diffusion with the B,C film. This compact structure also prevented the Mg-Al alloy film to merge with Al₂O₃.

To summarize, the sputtering pressure during the Mg-Al alloy film deposition is closely related to the looseness of the Mg-Al alloy film and the microstructure of thin films. The difference in the microstructures results in the difference in the adhesion of B,C films. Moreover, it is proved that a porous Mg-Al alloy film can immensely help to enhance the adhesion of B,C films through diffusion between layers without substrate-heatings.

3 Conclusions

B,C films with Mg-Al alloy films as the adhesive layers were deposited on Al substrate using the DC magnetron sputtering technique without substrate-heatings. 4 and GIXR, TEM, and SEM were used to investigate the effect of the Mg-Al alloy film on microstructures and interfaces of thin films. The experimental results show that a B,C film with a relatively low stress can be obtained at the sputtering pressure of 1.33 Pa during the B,C film deposition, and a porous and thin Mg-Al alloy film can more easily diffuse with both B,C film and Al₂O₃ to enhance the adhesion of the B,C film on Al substrate. In conclusion, by adding a 15 nm thick Mg-Al alloy film between Al substrate and the B,C film, and by increasing the sputtering pressure during the deposition of the B,C film and the Mg-Al alloy film, a B,C film of thickness 1.2 μm can be coated successfully on a commercial Al substrate without substrate-heatings. Hence, this paper provides useful guidance for further research and development of boron-coated neutron detectors.

References:


