Stress and adhesion of B_4C films for boron-coated neutron detectors

Feng Qinxu, Qi Runze, Li Wenbin, Ni Hangjian, Huang Qiushi, 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 ^{3}He neutron detectors, boron-coated neutron detectors have been a current focus for researchers worldwide. For the boron-coated neutron detectors, a B_4C film with low stress and good adhesion to the Al substrate is required. To enhance adhesion of the B_4C films on Al substrates, a B_4C film with low stress was fabricated by direct current sputtering technique without substrate-heating. The Mg-Al alloy thin film was introduced between the B_4C film and its substrate for enhancing the adhesion. The effect of sputtering pressure on the stress of B_4C films during deposition was studied. Additionally, the adhesion of B_4C 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 B_4C films decreases and stabilizes when sputtering pressure increases during deposition. Thin and porous Mg-Al films react well with both B_4C films and Al_2O_3 on Al substrates to enhance adhesion of the B_4C films, without substrate-heating.

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

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涂硼中子探测器用 B_4C 薄膜的应力和粘附力研究

冯秦旭，齐润泽，李文斌，倪航剑，黄秋实，张 众，王占山

(同济大学 物理科学与工程学院 精密光学工程技术研究所
先进微结构材料教育部重点实验室，上海 200092)

摘 要： 涂硼中子探测器作为 ^{3}He 中子探测器的替代技术，已经成为了当今研究的焦点。对于涂硼中子探测器而言，B_4C 薄膜的应力需要减小，与铝基底间的粘附力需要增大。为了增大 B_4C 薄膜与铝基底间的粘附力，该实验使用直流磁控溅射技术在不使用基底加热的前提下制备应力较小的 B_4C 薄膜，同时在铝基底和 B_4C 薄膜之间添加 Mg-Al 合金层。该实验主要研究了沉积过程中溅射气压对 B_4C 薄膜应力的影响，以及 Mg-Al 合金层及其溅射气压和厚度对 B_4C 薄膜粘附力的影响。实验结束后采用扫描电镜和透射电镜对薄膜的微观结构进行了表征和分析。实验结果表明，当沉积过程中溅射气压增大时，B_4C 薄膜的应力减小并趋于稳定。超薄多孔的 Mg-Al 合金层与 B_4C、

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作者简介： 冯秦旭(1994-)，男，硕士生，主要从事中子多层膜方面的研究。Email: 1631912@tongji.edu.cn

导师简介： 张众(1977-)，男，教授，博士生导师，博士，主要从事中子及 X 射线多层膜方面的研究。Email: zhangzhongcc@tongji.edu.cn

Al_2O_3 有着明显的反应,能够在不使用基底加热的前提下有效地增大 B_4C 薄膜与铝基底间的粘附力。
关键词: 涂硼中子探测器; 应力; Mg−Al 合金薄膜; 粘附力

0 Introduction

As an alternative to ^{3}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[1]. Generally, the neutron detector based on ^{3}He is the main equipment used for neutron detection. However, the limited supply and extensive consumption of ^{3}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 γ cross section, the boron−coated detector is used as an alternative for neutron detection[2].

To manufacture the boron−coated detector, a thick B_4C 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_4C film of thickness 1.2 μm was selected to be coated in this research[5]. 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 [6]. 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_4C film on Al substrate is very poor. B_4C 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_4C film with good adhesion without substrate−heating is studied. In this technique, a thick B_4C film with low stress is required to prevent peeling off[9]. Additionally, the adhesive layer between the B_4C 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_4C layer is essential. As reported in previous studies, a few active metals, such as Ti and Mg, can react with both Al_2O_3 and B_4C[11]. In this paper, the Mg−Al alloy film was selected as the adhesive layer for the better adhesion between B_4C film and Al substrate than Ti or Mg.

This paper focuses on the study of the stress and adhesion of B_4C 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_4C film and the Mg−Al alloy film. An appropriate method is proposed to coat a 1.2 μm thick B_4C film on a commercial Al substrate for the boron−coated detector.

1 Experiments

In this research, the Mg−Al alloy film and the B_4C film were deposited on the commercial aluminum substrates (Model: AA 1060) of dimension 10 mm×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 3×10^{-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_4C were 5.733 Å/s and1.0953 Å/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_4C 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_4C layer were determined[12]. The stress measurements were carried out on the B_4C 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:

$$\sigma_f=(1/R_{\text{post}}-1/R_{\text{pre}})(E_S/(1-V_S))t_S^2/6t_f \tag{1}$$

where t_S is the substrate thickness, t_f is the film thickness, and R_{pre} and R_{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_4C film on Al substrate qualitatively[13]. 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_4C films, the effect of the sputtering gas pressure on the film stress was studied. The B_4C 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_4C films is shown in Fig.1. The compressive stress of the B_4C 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.

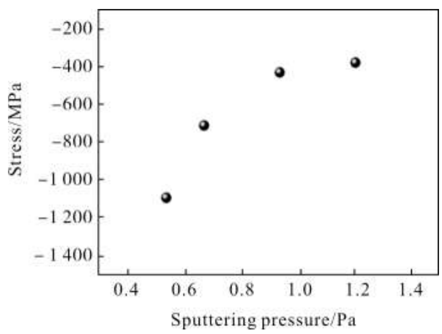

Fig.1 Stress results of B_4C films deposited at four different sputtering pressures of 0.53, 0.67, 0.93, and 1.20 Pa

The B_4C film usually becomes porous at a high sputtering pressure due to the decrease in the mean free path of gas molecules [14]. This porous structure leads to more defects in the B_4C 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_4C film deposition, the lower the stress of the B_4C film is.

2.2 Adhesion experiments

To enhance the adhesion of the B_4C 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_4C 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.

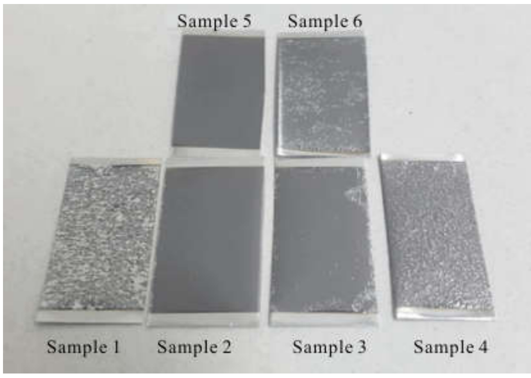

Fig.2 Picture of six samples deposited under different parameters after coating

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.

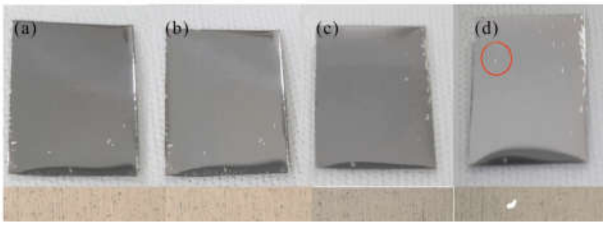

Fig.3 Pictures and micrographs of (a) Sample 2 before bonding, (b) Sample 2 after bonding, (c) Sample 5 before bonding, and (d) Sample 5 after bonding

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 SiO_2 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_4C film indicates

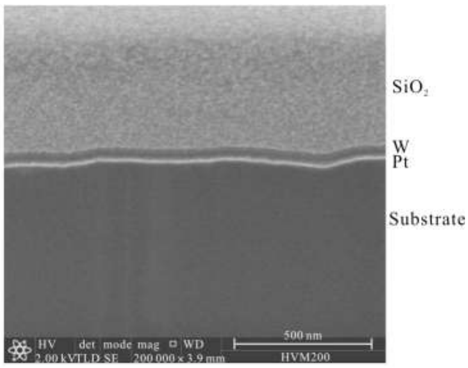

Fig.4 Cross-sectional SEM micrograph of the white spot

that the appearance of the white spot was due to the disconnection of the Mg–Al alloy film from Al_2O_3.

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 B_4C film can effectively enhance the adhesion of B_4C films. Secondly, the thickness of the Mg–Al alloy film should not be too thick. In this paper, the best adhesion of B_4C 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 B_4C films. The higher the sputtering pressure, the stronger the adhesion of B_4C films is. Thus, a relatively thin Mg–Al alloy film deposited at a high sputtering pressure can increase the adhesion of a B_4C film on Al substrate without substrate–heating.

2.3 Transmission electron microscopy

To further study the internal microstructure of B_4C 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 B_4C film, the diffusion layer between the Mg–Al alloy film and B_4C film, the mixture of the Mg–Al alloy film and Al_2O_3, 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 Al_2O_3 was strong. In Fig.5 (b) of Sample 5, each layer from top to down is the B_4C film, the Mg–Al alloy film, Al_2O_3, and Al substrate. There is a clear interface between each layer. Diffusion between the Mg–Al alloy film and B_4C film was weak. A clear stratification between the Mg–Al alloy film and Al_2O_3 clearly illustrated that there was a small amount of diffusion between them.

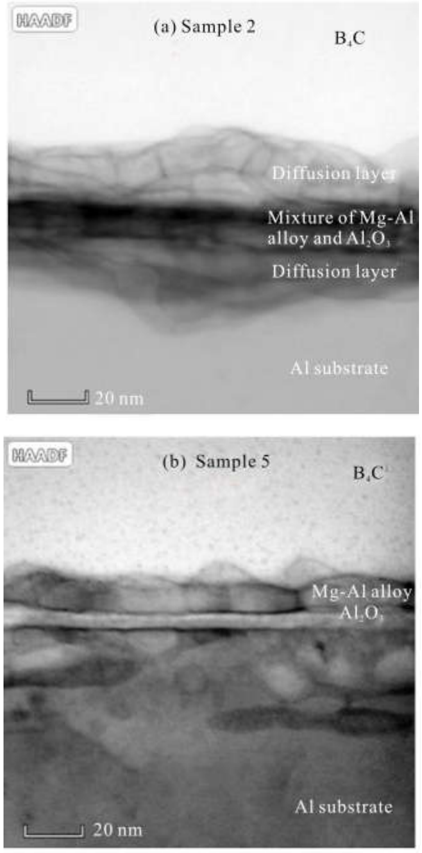

Fig.5 Bright–field cross–sectional TEM micrographs of (a) Sample 2 and (b) Sample 5

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[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_4C film and Al_2O_3. The Mg–Al alloy film for Sample 5 was compact, and hence, it had a weak diffusion with the B_4C film. This compact structure also prevented the Mg–Al alloy film to merge with Al_2O_3.

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_4C films. Moreover, it is proved that a porous Mg–Al alloy film can immensely help to enhance the adhesion of B_4C films through diffusion between layers without substrate–heating.

3 Conclusions

B_4C films with Mg–Al alloy films as the adhesive layers were deposited on Al substrate using the DC magnetron sputtering technique without substrate–heating, 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_4C film with a relatively low stress can be obtained at the sputtering pressure of 1.33 Pa during the B_4C film deposition, and a porous and thin Mg–Al alloy film can more easily diffuse with both B_4C film and Al_2O_3 to enhance the adhesion of the B_4C film on Al substrate. In conclusion, by adding a 15 nm thick Mg–Al alloy film between Al substrate and the B_4C film, and by increasing the sputtering pressure during the deposition of the B_4C film and the Mg–Al alloy film, a B_4C film of thickness 1.2 μm can be coated successfully on a commercial Al substrate without substrate–heating. Hence, this paper provides useful guidance for further research and development of boron–coated neutron detectors.

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