

Characterization of Tritium Retention in Plasma Sprayed B₄C/Mo Coatings

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Abstract: Quantification of the amount and depth of tritium retained on plasma facing materials (PFMs) surface is of great importance for selecting PFMs with high safety in the nuclear system. In the present study, potential PFMs of B₄C/Mo coatings were prepared and the depth profiles of tritium in the coatings were measured both by imaging plate (IP) technique and β -ray induced X-ray spectrometry (BIXS). The IP images showed that the amount of adsorbed tritium in the coatings followed the order of B₄C > BM15 > BM5 > Mo, which was along with the X-ray spectra also illustrating that most tritium penetrated into the bulk of the B₄C coating while on the surface only for the other three coatings. The cross-sectional morphologies of the coatings were observed by scanning electron microscope (SEM), which demonstrated that B₄C coatings had the highest porosity while the other three coatings were denser despite of the existence of smaller-sized pores and cracks. All the results suggest that pores and microcracks in the as-sprayed coatings provide passageway for tritium penetration and adsorption, which are the key factors that affect the amount of tritium adsorbed. Furthermore, the content of Ti contamination in the coatings also plays an important role in controlling tritium adsorption.

Key words: B₄C/Mo coatings; PFMs; tritium; X-ray spectrometry

In recent years, many researches have focused on energy issues related to solar energy and wind energy due to a global concern of energy shortage. As nuclear energy gradually plays an important role in our daily life, new nuclear plants are being established in many developed and developing countries to meet the growing energy requirement^[1-4]. Plasma facing materials (PFMs) are among the key factors that determine the quality of the whole fusion device, which ensure the safety of maintenance work in nuclear plants^[5-7].

A variety of techniques have been used for the quantification of hydrogen isotopes retained on the surface of PFMs, such as accelerator mass spectrometry (AMS)^[8], full-combustion method^[9], and charged-coupled device (CCD) camera tomography^[10]. Recently, a novel non-destructive instrument, so-called β -induced X-ray spectrometry (BIXS), has been developed for quantifying tritium concentration distribution both near-surface and in

bulk of the PFMs *via* separate computer simulation^[11-18]. This instrument has practical value for evaluating the tritium uptake into materials due to gas exposure or ion implantation processes^[18].

The majority of PFMs are carbide-based materials and high-density metals such as tungsten^[19-22]. As compared with bulk materials, the preparation of coatings is more economical and flexible. As a result, a lot of work has been focused on the attempt to find new PFMs. SiC and B₄C coatings are promising candidates for PFMs due to their high melting point as well as good thermal conductivity and high strength^[23-26]. Being a high atomic number material, molybdenum is also considered as a potential PFM^[27-28]. The melting point of molybdenum is up to 2625°C, at room temperature, forming an oxide film on the surface and passivation. It has a high ability to resist in acid, alkali and the molten metal. Molybdenum has a self-adhesive properties, can be combined with many metals. In addition,

Received date: 2013-01-31; Modified date: 2013-03-05; Published online: 2013-03-28

Foundation items: Open Fund of Key Laboratory of Inorganic Coating Materials, Shanghai Institute of Ceramics, Chinese Academy of Sciences(KLICM-2012-03); Research Fund for Nanomaterials of Shanghai (11nm0506900); Shanghai Municipal Committee of Science and Technology Research Project (11231201302); International S&T Cooperation Program of China (2013DFG52290)

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Molybdenum coating can be used as adhesive primer, and functional coating.

In the present study, four types of B₄C/Mo-based composite coatings were exposed to tritium gas. BIXS was employed to characterize the quantity of tritium retention in these coatings. The adsorption amount and depth profile of tritium were also investigated for these materials.

1 Materials and Methods

1.1 Materials

To examine the tritium exposure, four types of B₄C/Mo-based composite coatings on the substrate of stainless steel (15 mm×15 mm×2 mm) were prepared by vacuum plasma spraying (VPS). The spraying parameters were shown in Table 1. Mo coating was pure metal coating, its spraying parameters was different from the B₄C/Mo-based composite coatings. All samples were rinsed in acetone, and then baked at 120°C for 5 h, 200°C for 2 h, 250°C for 2 h, 300°C for 4 h, 350°C for 2 h and 400°C for 4 h under high vacuum conditions ($<3 \times 10^{-4}$ Pa). The vacuum pressure eventually reached an order of 10^{-6} Pa.

1.2 Experimental methods

1.2.1 Exposure and BIXS measurement

All coating samples were exposed to tritium gas (tritium concentration 5% T) under given temperature (673 K), pressure (2.6 kPa) and time (4 h). The amount of tritium retained in the surface layers of the samples was determined by BIXS with argon as the working gas^[18].

Table 1 Vacuum plasma spraying parameters

Parameters	B ₄ C	Mo
	BM5(95vol%B ₄ C-5vol%Mo) BM15(85vol%B ₄ C-15vol%Mo)	
Current/A	620	600
Ar gas flow/srpm	37	40
H ₂ gas flow/srpm	13	12
Carrier gas flow/srpm	2.5	3
Powder feed rate/(r • min ⁻¹)	22	18
Spray distance/mm	220	180
Pressure/Pa	40000	50000

1.2.2 Imaging plate

The imaging plate (IP) technique, which was developed for the detection of low energy β -rays such as those generated by tritium, was performed to characterize the surface tritium activities of the four coating samples. The IP (BAS-TR2025, Fuji Photo Film Co. Ltd, Japan) was first placed in contact with each coating sample for 15 min in a dark shielded room, and then processed by an imaging

plate reader (BAS-2500, Fuji Photo Film Co. Ltd, Japan) to obtain the digitized photon-stimulated-luminescence (PSL) intensity pattern as well as a two-dimensional mapping. The PSL intensity is a measure of the adsorbed energy in the IP, which cannot be directly converted to absolute tritium level but is nearly proportional to the tritium surface concentration. Details of tritium detection by IP technique are available elsewhere^[29-31].

2 Results and discussion

2.1 Imaging plate

Figure 1 shows the distribution of tritium in the four types of coating samples. A higher tritium level is shown in red and a lower level in blue^[31]. As can be seen, the surface of the B₄C coating showed a red color, indicating substantial tritium adsorption. The surface of the Mo coating showed a blue color, demonstrating the smallest amount of adsorbed tritium comparing with the other coatings. For all the samples investigated, tritium adsorption followed the order of B₄C>BM15>BM5>Mo.

2.2 X-ray spectra of alloys

Figure 2 shows the X-ray spectrum for the B₄C coating and associated changes peaks of the elements within the B₄C coating with time up to 1 h. Five X-ray peaks were observed in the spectrum, one of which corresponding to Ar(K α) was sharp and intense, with the maximum intensity appeared at 2.99 keV. Cr(K α), Fe(K α) and Ni(K α) peaks were also observed, which were common since the substrate was stainless steel. However, the Ti(K α) peak was not expected. Also the X-ray energies for C and B were too small to be observed. The considerably broad, strong spectrum of bremsstrahlung X-rays indicated that the tritium adsorbed at the surface of B₄C coating was potentially diffused into the bulk material^[18].

Figure 3 shows the X-ray spectra of BM5, BM15 and Mo coatings. For these three spectra, only sharp peaks were observed with no clear bremsstrahlung X-ray peaks. This indicated that most tritium was probably only adsorbed on the surface of these coatings.

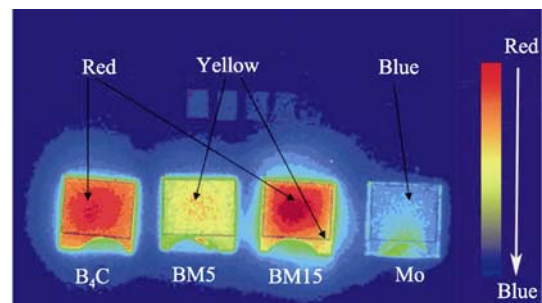


Fig. 1 IP image of the coating samples

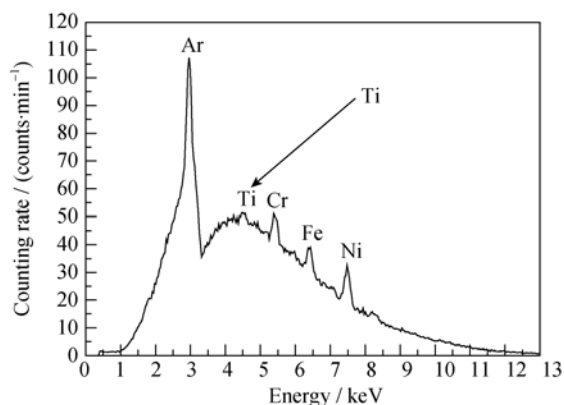


Fig. 2 X-ray spectrum of the B₄C coating

Figure 4 shows the cross-sectional morphologies of the four types of coatings. As can be seen, there were a large number of pores in the B₄C coating, ranging from several to 30 μm in size. Comparing with the B₄C coating, the BM5 and BM15 coatings were much denser, since molybdenum occupied most of the big pores (Mo was indicated by the bright area, as shown in Fig.4(b) and (c)). Since the porosity of the Mo coating was the lowest (30%, 8.2%, 6.4% and 2.4% for B₄C, BM15, BM5 and Mo coatings, respectively), which also showed the smallest amount of tritium retention, it could be inferred that it must be the

dense coating regardless of the physical and chemical properties that counts for the low adsorption of tritium.

Table 2 summarizes the intensities of Ar(K α) and Ti(K α) peaks in the spectra of the four coatings. The results showed that the net counting rates of Ar(K α) for the BM5, BM15 and Mo coatings were much lower than that of the B₄C coating, which was in accordance with the results from IP images, indicating that the retaining amount of tritium on the surface of these three coatings were dramatically smaller than that of the B₄C coating. Interestingly, the intensities of Ar(K α) peaks in the X-ray spectra were almost the same for both of the BM5 and BM15 coatings, while that of the Ti(K α) peak for the BM5 coating was approximately 1/30 of that for the BM15 coating only. This demonstrates that the containing of Ti contamination is also one of the key factors that determine the absorption of tritium into the coatings.

The B₄C coating has already been successfully applied as first wall materials, indicating that B₄C possesses many good properties. However, in the present study the B₄C coating showed the highest tritium retention, which should be attributed to the high porosity of the coating. It is known that tritium can be in contact with coatings in the form of gas. Thus, tritium can easily penetrate into the

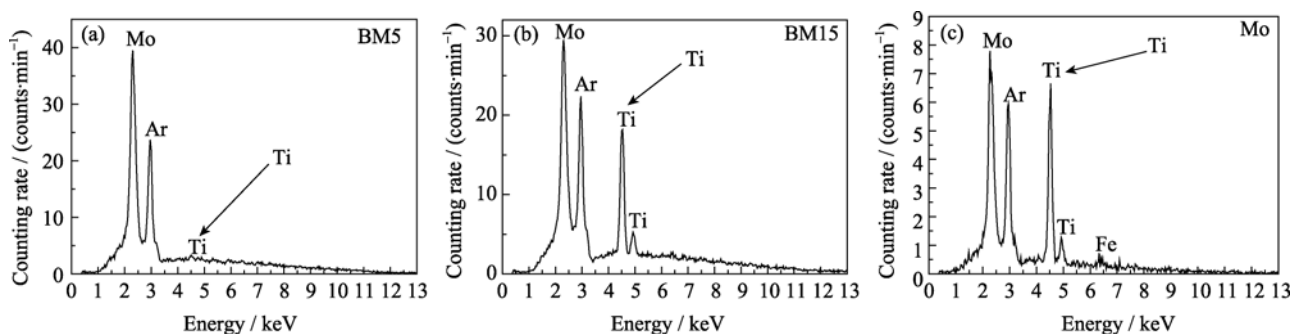


Fig. 3 X-ray spectra for coatings (a) BM5; (b) BM15; (c) Mo

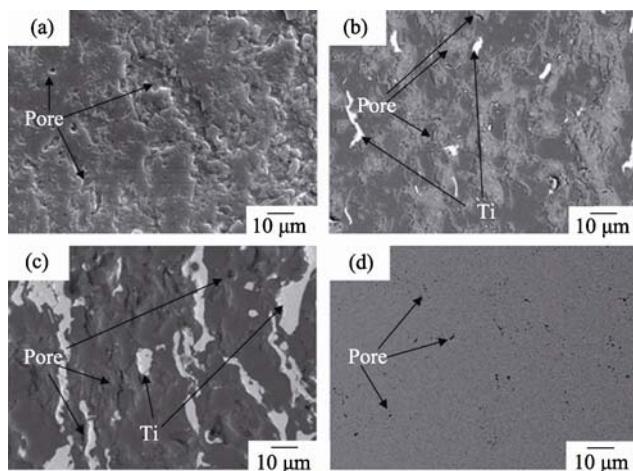


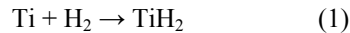
Fig. 4 Cross-sectional morphologies of coatings (a) B₄C; (b) BM5; (c) BM15; (d) Mo

coating through pores and finally be adsorbed in them. Similarly, a study by Wu^[18] has demonstrated that the intensity of Ar(K α) peak for the Pc-W coating with compact structure is only 1/4 of that for the VPS-W coating with inevitable voids or pores. The big pores, especially those above 10 μm in size can provide channels for tritium gas permeation and space for tritium storage. Besides, as for the case of BM5 and Mo coatings, the porosity of which is less than 5%, the nano-sized cracks are still inevitable due to the thermal spraying process, which may also provide rapid absorption passageway for tritium. However, since the speed of tritium absorption through nano-sized cracks is much lower, the net counting rate of Ar(K α) for B₄C coating was substantially higher than those of the other coatings.

Table 2 Net counting rate of four composite coatings

Net counting rate / (counts • min ⁻¹)	B ₄ C	BM5	BM15	Mo
Ar(K α)	1344.54	113.74	118.73	29.86
Ti(K α)	23.27	3.62	109.47	31.63

In addition to cracks and pores, other factors may also determine the amount of tritium adsorbed. For the coatings whose porosity is less than 5%, the content of Ti contamination should be another important factor that determines the absorption of tritium. Ti is very active to react with tritium:



For the coatings investigated, the intensities of main peaks (K α and K β) of titanium were strong even when the Ti content was low, indicating that the solubility of tritium in Ti was relatively high.

3 Conclusion

In this study, four types of B₄C/Mo-based composite coatings were fabricated by vacuum plasma spraying. The results showed that the pure B₄C coating retained the highest amount of adsorbed tritium, as its porous structure allowed deeper tritium diffusion into the bulk material, while the pure Mo coating showed the lowest adsorption of tritium.

The pores and microcracks provide passageway for tritium penetration and are the key factors that determine the amount of tritium adsorbed by the coatings. The content of Ti contamination is another important factor that controls the adsorption of tritium into the coatings. Due to the inevitable cracks and pores, thermal spraying technology is not suitable for PFMs candidate selection.

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等离子喷涂碳化硼/钼涂层氘的滞留性能研究

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摘要: 为了保证核能源的使用安全, 对氘在第一壁材料表面的滞留数量以及深度进行定量表征非常重要。在本研究中, 制备了一系列潜在的第一壁材料 B₄C/Mo 涂层, 并采用成像板(IP)和 β 射线激发 X 射线(BIXS)法对其表面的氘滞留情况进行了测定。IP 图像表明, 涂层表面吸附的氘含量遵循以下顺序: B₄C>BM15>BM5>Mo。而 BIXS 结果进一步表明, 对于 B₄C 涂层, 大部分氘扩散到了涂层内部; 而对于其他三种涂层, 氘仅在其表面发生吸附。扫描电镜(SEM)结果显示, B₄C 涂层气孔率最高, 而其他三种涂层尽管气孔率较低, 但其截面仍能观察到大量气孔和微裂纹的存在。涂层中的这些缺陷为氘的吸收和扩散提供了通道, 而气孔与微裂纹的尺寸最终决定了氘在涂层表面的吸附数量。实验结果还表明, 涂层杂质成分 Ti 的存在也对氘的滞留产生了一定影响。

关键词: 碳化硼/钼; 第一壁材料; 氘; X 射线光谱法
中图分类号: TG174 文献标识码: A