

Effect of heat treatment on surface composition of hydrogen implanted C–SiC coatings

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Abstract: C–SiC coatings were prepared on stainless steel substrate by the middle frequency magnetron sputtering (MFMS) and ion beam mixing technique. After deposition, these samples were implanted by 5 keV hydrogen ion beam at a dose of 1×10^{18} ion/cm². Some samples were heat treated at different temperatures from 273 K to 1173 K separately. The surface morphology, surface concentration of the elements of the C–SiC coatings and element iron from substrate as well as their depth profiles were checked with SEM, XPS and SIMS analyses. The results show that the composition of the coatings is changed due to heat treatment at different temperatures. The C–50%SiC coating with an excellent hydrogen resistant property can act as hydrogen barrier at the temperature below 723 K. But the hydrogen resistant property of the coating becomes bad when it is used at the temperature of 1023 K.

Key words: C–SiC coating; hydrogen implantation; heat treatment

1 Introduction

Due to silicon carbide (SiC) with large band gap, the possibility to dope it into n-type or p-type permits its electronic applications [1]. SiC and C–SiC with their good thermal conductivity, thermal shock resistance and excellent hydrogen resistant are regarded as protective surface coatings used on the first wall of magnetic confinement fusion device and on the inside of nuclear waste barrels which store radioactive waste of hydrogen isotopes [2,3]. They can also be used as brake materials [4]. Such coatings on substrate can effectively protect the nuclear waste barrels from the overflow of the harmful radioactive waste like tritium at the complicated environment when the barrels with full radioactive waste are buried to understand at high temperature under their irradiation conditions. It is known that the carbide is susceptible to chemical sputtering under energetic hydrogen irradiation resulting in the production of methane and other hydrocarbon species [3]. In addition, the interaction between C–SiC and elements of the radioactive waste is very complicated. For example,

species like hydrogen isotopes and their transmutation products like helium can be trapped in the C–SiC coatings within the holes, grain boundary and interstitial sites. And they can also be de-trapped at high temperature when they get enough kinetic energy and these species like gases can migrate to the surface and escape from the surface. So, the escaped species may contain some elements of the coatings [5]. In other words, the loss of C–SiC coatings happens not only during coating preparation with energetic process but also during storing radioactive waste time. The degree in the loss of C–SiC coatings in the storing duration depends on the environmental conditions. It has been reported that a large amount of implanted hydrogen is contained in the form of molecules, or C–H and Si–H compound in the bubbles and some of hydrogen atoms implanted in SiC are trapped in both Si- and C-sites [6].

In this work, hydrogen ions implanted C–SiC coatings prepared on stainless steel were heat treated at different temperature, and SEM, XPS and SIMS analyses were used to characterize the changes of the coating composition at different temperatures.

2 Experimental

The substrates made of 1Cr18Ni9Ti stainless steel with dimensions of $d10\text{ mm}\times 4\text{ mm}$ were polished and then degreased in benzene using ultrasonic cleaning, rinsed in de-ionized water and finally dried. Before deposition the sputter cleaning with Ar^+ ion was used in order to clean the sample surface, which can considerably improve the adhesion of the deposited films to the cleaned surface of the substrate. C–50%SiC films were prepared on stainless steel substrates by the middle frequency magnetron sputtering (MFMS). The chamber had a base pressure of $4\times 10^{-4}\text{ Pa}$, and this pressure was increased to about 0.5 Pa during film deposition due to the argon gas in the discharge [7]. The thickness of the C–SiC films was about 200 nm. Then these samples were vertically implanted by H^+ beam with energy of 5 keV at a dose of $1\times 10^{18}\text{ ion/cm}^2$. The vacuum during hydrogen ion implantation was about 4 mPa. After the hydrogen ion implantation, some samples were put into the furnace. The furnace was evacuated to the vacuum of 6 mPa. After that, the heat treatment process was started under flowing gas of Ar at 573, 873, 1023 and 1173 K, respectively. Each process lasted for 30 min isothermally. The heating rate from RT to the designed temperature was 10 K/min during the process and then the sample was naturally cooled with the furnace. A schematic diagram of such a heat treatment procedure is shown in Fig. 1.

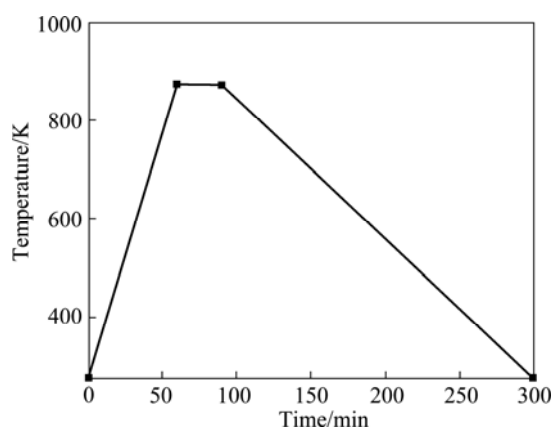


Fig. 1 Schematic of heat treatment procedure

Secondary ion mass spectroscopy (SIMS) with an IMS-4F system of CAMECA operation was used to measure the element depth profiles in the film and interface area. During SIMS measurement, O_2^+ beam with 15 kV and 200 nA was used to peel the top layer on the surface of the samples in order to measure the sub-layer composition. A JSM-5610LV instrument was used for the SEM observation with an accelerating voltage 20 kV. X-ray photoelectron spectra of the surface composition were obtained using KRATOS-XSAM800

surface analysis system with mono-chromatic Al K_{α} radiation (1486.6 eV) operating at 13 kV and 19 mA.

3 Results and discussion

Figure 2 shows the SEM surface morphologies of the C–50%SiC coatings prepared by MFMS and ion-beam mixing in as-deposited state and after argon deletion. It can be found that the coating surface seems uniform. While bubbles with different sizes appear after heating at 673 K for 30 min in order to remove argon gas which was used as an auxiliary gas during coating preparation by MFMS technique.

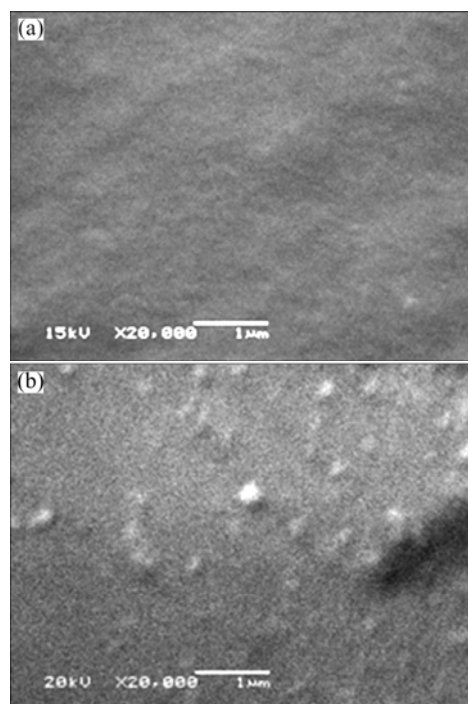


Fig. 2 Surface morphologies of C–50%SiC coatings obtained by MFMS technique: (a) As-deposited; (b) After argon deletion with heating at 673 K for 30 min

Figure 3 shows the SEM surface morphology of the argon removed C–50%SiC coatings after hydrogen ion implantation with 5 keV and $1\times 10^{18}\text{ ion/cm}^2$. It can be seen that the bubbles on the surface are broken. Hydrogen ion implantation leads to rupture of the bubbles due to the fact that some suitable energetic hydrogen particles can react with C or Si of the coatings to form gaseous species [8,9], at the same time, hydrogen ion irradiation can enhance the migration of these species. They move to the bubbles together with argon in the bubbles causing the pressure increasing rapidly, and finally, the bubbles are broken when the pressure in the bubble is large enough and surpasses the surface tension.

Figure 4 shows the SEM surface morphologies of the hydrogen ion implanted C–50%SiC coatings after heating at 573, 873, and 1173 K. It can be found that the

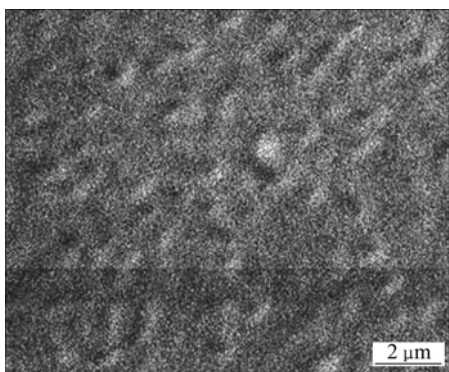


Fig. 3 SEM surface morphology of hydrogen ion irradiated C-50%SiC coating

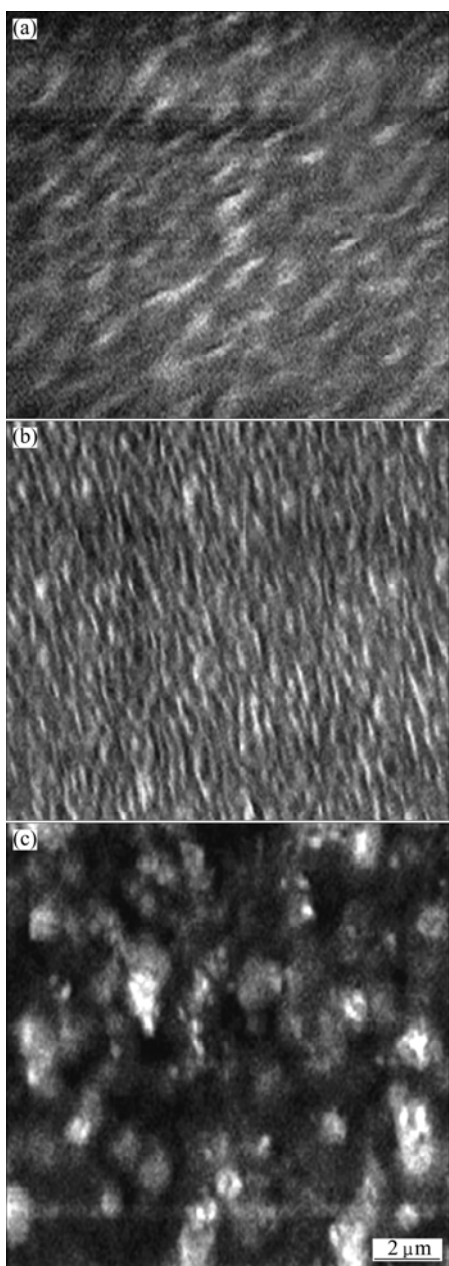


Fig. 4 SEM morphologies of hydrogen implanted C-SiC coatings after heat treatment at 573 K (a), 873 K (b) and 1173 K (c)

amorphous C-SiC coating has changed to aggregated and crystallized after heat treatment. And the surface morphologies show different morphologic features at different heating temperatures. An interesting phenomenon is that the arrangement of the granule on the surface is along with a certain orientation (Fig. 4(a)), and the surface morphology exhibits different orientations at different heating temperatures (Fig. 4(b)), but such a feature seems to disappear after heating at 1173 K (Fig. 4(c)). Another inconceivable phenomenon is that the size of the granule on the surface of C-SiC coating annealed at 873 K is smaller than that at 573 K, which may be related to the orientation of crystallite. The surface morphology after heating at 1173 K shows completely different feature that it become spherical-like, which may mean the loss of the C-SiC coatings.

Figure 5 shows the XPS spectrum on the surface of the deposited C-SiC coatings by MFMS technique. It can be seen that there exists naturally adsorbed or oxidized contamination on the top layer. Some contaminations came from the residue gases, such as CO, CO₂ and H₂O, in the vacuum chamber during coatings deposition [10] and some from air when the samples were placed in air. Apart from those contaminations, there also exist elements of the coatings, such as C, Si and auxiliary argon. The similar XPS spectra can be obtained for the C-SiC coatings after heating, where the thickness of the contamination lay is 6–15 nm.

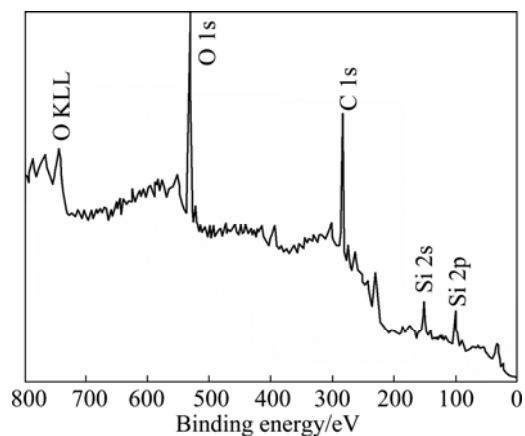


Fig. 5 XPS spectrum over a wide energy range on surface of C-SiC coating

Figure 6 shows the change of the C and Si concentration on the surface of the C-SiC coatings determined by EDAX analysis. The change of C to Si mole ratio is also reported in the inset of Fig. 6. It can be seen that the concentration of Si decreases with increasing heating temperature, while that of C is almost unchanged during heating at 273–723 K, and then decreases after heating above 723 K. The mole ratio of C to Si on the surface shown in the inset is 3.2 for the as-

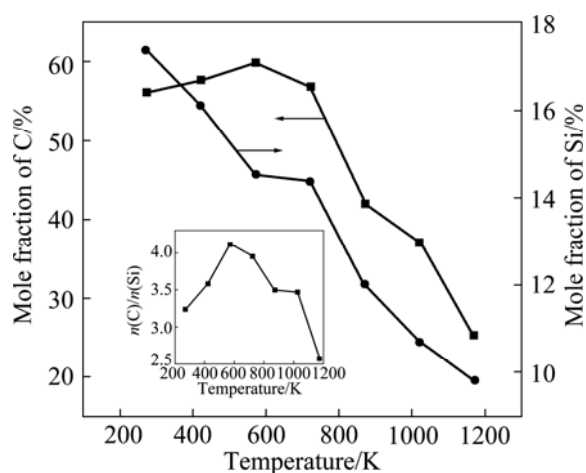


Fig. 6 Ratio of C and Si as well as mole ratio of C to Si on surface related to heating temperature by EDAX analysis

deposited C–SiC coating, increases after heating at 273–723 K, then decreases from 4.1 to 3.5 after heating at 723–873 K and maintains 3.3 at 873–1023 K, finally, it decreases to be smaller than 3.2 at 1173 K. This can be explained that at the temperature of 273–573 K, Si concentration decreases while the contamination, like oxygen or carbon, increases, leading to C concentration invariance even increase a little. Such a result causes the increase of the mole ratio of C to Si. At the temperature of 573–873 K, the contaminations are gradually volatile, which causes the decrease of the C concentration, while the concentration of Si decreases slowly at 573–723 K then quickly at 723–873 K. This leads to the mole ratio of C to Si decrease slowly at 573–723 K. At 873–1023 K, the concentrations of Si and C decrease with the similar speed, leading to the mole ratio of C to Si almost unchanged. At 1023–1173 K, the concentration decrease in C is faster than that in Si, leading to the mole ratio of C to Si decreasing quickly. Based on Fig. 6, it can be found that after heating at 1023 K, the mole ratio of C to Si is 3.3, close to the balance of 3.2. This infers that C–50%SiC coatings still remains, but, the amount only seems to be half the original one. Obviously, dilution of the C–SiC coatings is due to elements like Fe entering into them and consumption of the elements C and Si of the C–SiC coatings, leading to the gross of C and Si decreasing rapidly after heating above 1023 K.

Figure 7 show the SIMS depth profiles of elements C, Si and Fe for the samples before and after heat treatment at different temperatures. Several features can be seen as follows.

1) The SIMS depth profiles of C and Si for the as-prepared C–SiC coating show that there exist two parts: one part is the plateau showing the body of the C–SiC coating, where the width of the plateau represents the thickness of the C–SiC coating, and another is the

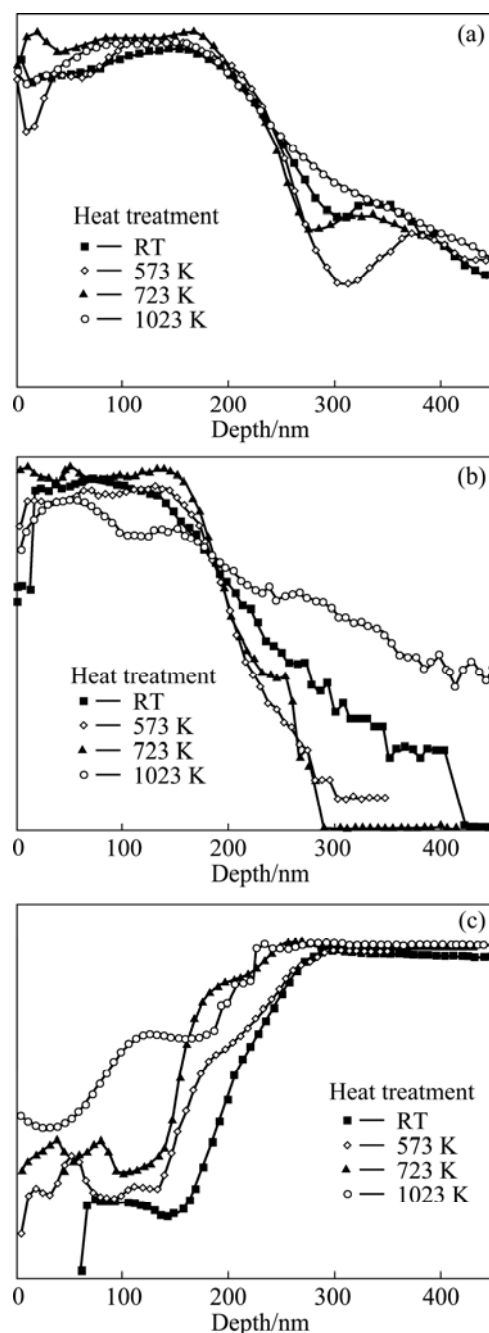


Fig. 7 SIMS depth profiles of C (a), Si (b) and Fe (c) before and after heating at different temperatures

interface layer between the C–SiC coating and substrate. It can be seen that the C–SiC coating has a good adhesion to the substrate based on the interface layer with composition mixing between the C–SiC coating and substrate.

2) The top layer on the surface of the C–SiC coating shows that the natural carbon contamination leads to higher C concentration for the as-deposited C–SiC coating. The natural carbon contamination is volatile after heating at 573 K, causing decreasing in the carbon concentration and increasing in the Si concentration. At 723 K, Si and C concentrations increase due to

contamination volatile. After heating at 1023 K, silicon-related species like Si–C–H, related gaseous species, are lost, leading to Si and C decreasing in the top layer [5,11].

3) The plateau of Si becomes flat with higher concentration in the corners, meaning Si migrating to the surface and the interface after heating at 573–723 K. Similar situation can be seen in C profile. After heating at 1023 K, collapse of Si depth profile in the side close to the interface happens, meaning large loss of Si concentration; while the Fe concentration in the C–SiC coating is increased and maintains at high level. But the width of the plateau of Si concentration still unchanged, representing that the C–SiC coating still exists. Combining with the results of Fig. 4(c), it manifests that the C–SiC coatings become loose and extra substance enters into the coatings. In other words, the C–SiC coatings seem difficult to undergo the environmental temperature of 1023 K.

4) The depth profile of Si at the interface area for the as-deposited C–SiC coatings shows that a lot of Si migrates into the substrate due to ion beam mixing effect during deposition process, where recoil collisions of energetic ions with atoms of coating and substrate leading to intermixing [12–14] enhanced inter-diffusivity [15,16]. These effects cause Si moving to substrate deeply. And Si in the interface migrates back to the coating after heating at 573–723 K due to the fact that the coating becomes denser; while a lot of Fe migrates to the interface and to the coatings with increasing heating temperature.

Figure 8 shows the SIMS depth profile of H after heat treatment at different temperatures. Hydrogen concentration in the C–SiC coating seems to not change after heat treatment at the temperature below 723 K. At 573–723 K, H in the interface migrates back to the coating with the similar tendency of element Si. Such a phenomenon means that H bonding to Si and C has

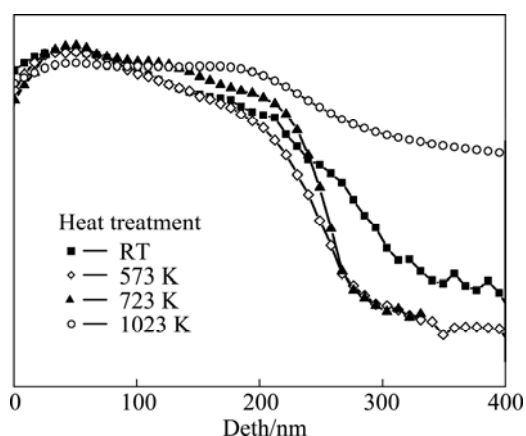


Fig. 8 SIMS depth profile of H after heat treatment at different temperatures

formed some species like Si–H_x and C–H_x. The SIMS depth profile of H after heating at 1023 K shows that most hydrogen moves to the substrate, meaning that the C–SiC coatings cannot act as the hydrogen isotopes barriers if they are used at the temperature of 1023 K.

4 Conclusions

1) Observation on the surface morphologies of the C–50%SiC coating before and after heat treatment shows that hydrogen ion implantation leads to the bubbles in the surface of the C–50%SiC coating. Amorphous structure of the C–50%SiC coating changes to crystallization after heat treatment and those granules on the surface arrange along with some orientation dependent on heating temperature. The spherical-like surface morphologies mean the loss of the C–SiC coatings after heat treatment at 1173 K.

2) The C–50%SiC coatings are excellent hydrogen barriers used at the temperature below 723 K. But they can not maintain hydrogen any more at 1023 K.

References

- [1] ZHU Xiao-min, YU Jia-kang, WANG Xin-yu. Microstructure and properties of Al/Si/SiC composites for electronic packaging [J]. Transactions of Nonferrous Metals Society of China, 2012, 22: 1686–1692.
- [2] BEREIARTU A, ORDÁS N, GARCIA C, MORONO A, HODGSON E. Manufacturing and characterization of porous SiC for flow channel inserts in dual-coolant blanket designs [J]. Fusion Engineering and Design, 2011, 86: 2526–2529.
- [3] OYA Y, ONISHI Y, KODAMA H, OKUNO K, TANAKA S. Dynamic hydrogen isotope behavior and its chemical states in SiC by XPS and TDS technique [J]. Journal of Nuclear Materials, 2005, 337–339: 595–599.
- [4] ZHANG J X, FAN S W, ZHANG L T, CHENG L F, YANG S J, TIAN G L. Microstructure and frictional properties of 3D needled C/SiC brake materials modified with graphite [J]. Transactions of Nonferrous Metals Society of China, 2010, 20: 2289–2293.
- [5] HUANG N K, YANG B. Behaviors of hydrogen in C–SiC films with IR and SIMS analyses [J]. Nucl Instr Meth B, 2002, 195: 344–349.
- [6] HOJOU K, FURUNO S, KUSHITA K N, SASAJIMA N, IZUI K. EELS analysis of SiC crystals under hydrogen and helium dual-ion beam irradiation [J]. Nucl Instr Meth B, 1998, 141: 148–153.
- [7] HUANG N K, WANG M H, SHEN Y. Multifunction equipment combining ion, electron and atom beams [J]. Meas Sci Technol, 1992, 3: 879–883.
- [8] REN D, DU J F, ZHANG R Q, YANG S Q, HUANG N K. Study in the effect of annealing on hydrogen retention properties of C–90%SiC films [J]. Surf Interface Anal, 2008, 40: 121–124.
- [9] WANG L W, YANG B, WANG D Z. IR and SIMS studies in 70% SiC–C films of hydrogen introduced with different methods [J]. Physica B, 2007, 389: 207–212.
- [10] HUANG N K, KHEYRANDISH H, COLLGON J S. Microstructure of zirconia films prepared by argon ion beam enhanced deposition [J]. Phys Stat Sol A, 1992, 132(2): 405–411.
- [11] OYA Y, ONISHI Y, OKUNO K, TANAKA S. Trapping and detrapping mechanisms of deuterium in SiC studied by XPS and TDS techniques [J]. Mater Trans, 2005, 46(3): 552–556.

- [12] SAVADORI M C, CATTANI M, VIZIR A. Metal ion mixing in diamond [J]. Surf Coat Technol, 2000, 128–129: 375–380.
- [13] NAKATANI R, TANIGUCHI R, CHIMI Y, ISHIKAWA N, FUKUZUMI M. Atomic mixing at metal-oxide interface by high energy heavy ions [J]. Nucl Instr Meth B, 2005, 230: 234–239.
- [14] BOLSE W. Mechanisms of ion beam induced atomic mixing in solid [J]. Mater Sci Eng A, 1998, 253(1–2): 194–201.
- [15] PARK J W, CHUN Y, CHANG J. Effects of ion beam mixing of silicon carbide film deposited onto metallic materials for application to nuclear hydrogen production [J]. J Nucl Mater, 2007, 362: 268–273.
- [16] ZHOU L P, WANG M P, PENG K, ZHU J J, FU Z, LI Z. Structure characteristic and its evolution of Cu–W films prepared by dual-target magnetron sputtering deposition [J]. Transactions of Nonferrous Metals Society of China, 2012, 22(11): 2700–2706.

热处理对注入氢离子的 C–SiC 涂层表面成分的影响

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摘 要: 采用中频磁控溅射结合离子束混合技术在不锈钢基体上制备 C–SiC 涂层。对制备的涂层进行能量 5 keV、剂量 1×10^{18} ions/cm² 的氢离子注入, 模拟涂层阻止氢渗透。之后, 分别将样品从 273 K 加入到 1173 K。采用 SEM、XPS 和 SIMS 分析表面形貌、表面成分及各元素的深度分布。结果表明, 不同温度的加热处理使涂层的成分发生变化, 在 723 K 以下温度处理时, C–50%SiC 涂层仍能保持非常好的氢阻止性能, 在 1023 K 以上温度处理时, 涂层不再具有阻氢性能。

关键词: C–SiC 涂层; 氢离子注入; 热处理

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