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Effect of sol-gel ZrO_2 films on corrosion behavior of the 304 stainless steel in coal-gases environment at high temperature

Jiao Yu[a], Guojun Ji[a,*], Quansheng Liu[a], Jianbin Zhang[a], Zhiming Shi[b]

[a] College of Chemical Engineering, Inner Mongolia University of Technology, Hohhot 010051, China
[b] College of Materials Science and Engineering, Inner Mongolia University of Technology, Hohhot 010051, China

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ABSTRACT

In this work, ZrO_2 films were prepared on 304 stainless steel surface through the sol − gel method by sintering at 600 °C. The crystal structure and the surface morphology of films were characterized by X-ray diffraction and X-ray photoelectron spectroscopy. The corrosion resistances of uncoated and coated specimens were studied by high-temperature corrosion tests. During the test, samples were exposure to CO_2-CO-CH_4-H_2-H_2S gases of coal during gasification at 600 °C, 700 °C and 800 °C. The results showed that corrosion pits and cracks in the stainless steel surface were caused by intergranular corrosion and thermal cracking. Furthermore, carbides and sulfides accelerated the intergranular corrosion of the samples, shortening the service life of the samples. No significant damage was observed on sample surfaces coated with ZrO_2 films at test temperatures of 600 °C and 700 °C. When this temperature was raised to 800 °C, the slight intergranular corrosion was observed on the sample surface. At 700 °C, carbides and sulfides did not react with zirconia under the normal oxygen partial pressure, protecting the stainless steel matrix and enhancing the corrosion resistance of the matrix.

1. Introduction

With the depletion of high-rank coals and petroleum, the use of low-rank subbituminous coal and lignite has been receiving increasing attention in the energy and mining industries [1]. Lignite is classified as low grade fuel, and generally featured with the high water content and the low sulfur content [2]. Lignite combustion produces a large amount of CO_2-CO-CH_4-H_2-H_2S gases [3,4]. Therefore, the problem of gas corrosion has become increasingly prominent. Stainless steel is extensively utilized in many chemical industries because of its excellent corrosion resistance and mechanical properties. The 304 stainless steel is the most common type of stainless steel because it exhibits good corrosion protection by the formation of passive films of chromium oxides on the surface that prevents the direct contact of the metal with an aggressive environment [5,6]. However, the internal precipitation of chromium-rich compounds and the repeated cycles of selective Cr_2O_3 scale formation and spallation reduce the protection performance of stainless steel at high temperature. When the protective chromium oxide scale fails and cannot heal because of chromium depletion, the alloy is susceptible to sulfur, oxygen and carbon attack. Moreover, the 304 stainless steel experiences segregation, hot cracking and intergranular corrosion at high temperature [7,8], which becomes more serious in a high carbon environment. Therefore, for improving these properties, coatings on steels is one of the most promising applications.

ZrO_2 films possess many excellent physical and chemical properties, such as good chemical stability and high strength, which make them an ideal protective coating against corrosion and wear. In recent years, ZrO_2 films have been widely used in industries, such as heterogeneous catalysis [9], photocatalysis [10], solar cells [11], chemical sensors [12], corrosion-protectives coatings [13] and biomedicine [14]. ZrO_2 has three polymorphic phases (stable at various temperatures): cubic, tetragonal and monoclinic. Among these phases, the stabilization of tetragonal ZrO_2 at room temperature for high-temperature applications has attracted considerable attention. ZrO_2 films have a high thermal expansion coefficient close to that of stainless steels. At present, ZrO_2 films can be prepared through chemical spray pyrolysis [15], electron beam evaporation [16], vapor deposition [17], sol-gel synthesis [18], pulsed laser deposition, and so on [19]. The sol-gel method has advantages such as low temperature and surface homogeneity. Thus, ZrO_2 films were prepared through the sol–gel method in this paper.

During the Lignite combustion, the main product gases are CH_4-H_2-CO-CO_2-H_2O-H_2S [20], which can be oxidized and carburized to stainless steel. Many studies have shown that stainless steel will undergo localized corrosion in a carbon environment [7,21,22]. In recent years, the relationship between corrosion rate and Cr content in carbon and carbon oxide environment has been studied depth. However, most

* Corresponding author.
E-mail address: jgj@imut.edu.cn (G. Ji).

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Table 1
Composition of 304 stainless steel substrates.

Element	Fe	C	Cr	Ni	Mn	Si	P	S
Mass percent	~71	0.032	18.0	8.65	1.28	0.62	0.031	0.01

Table 2
Chemical composition of the lignite.

Element	C	H	O	N	S
Mass percent	64.39	4.50	24.43	1.21	0.42

of these studies have focused on the properties of the steel, but there is little research in the direction of film protection. ZrO_2 films are more resistant to reactions with sulfides, carbon and carbon oxides in the case of normal oxygen partial pressures at 800 °C, which effectively prevents the gas from penetrating into the stainless steel. Thus, the ZrO_2 films can be used to protect the corrosion of stainless steel by sulfides, carbon and carbon oxides.

2. Experimental procedure

2.1. Materials and pretreatment

The 304 stainless steel specimens were machined into 20 mm × 10 mm × 1 mm samples, which sheets produced by Taiyuan Iron and Steel Group Co. Ltd. were used as substrates. The chemical composition of this material is given in Table 1. Before deposition, stainless steel mirrors were cleaned in an ultrasonic bath and rinsed in distilled water.

In this work, the simulation for the coal gasification process was performed. The stainless steel samples placed into the central zone of the simulation environment were pyrolized at 600 °C, 700 °C and 800 °C for 5 h, after which the corrosion morphology of the stainless steel was observed. The experimental coal was taken from the lignite of No. 2 mine in Shengli Coalfield, Xilinhot. The chemical composition of the lignite is given in Table 2. The lignite was dried at 102 °C for 6 h, and then it was ground and pulverized to a particle size of 0.5–1.0 mm. Finally, a volume ratio of H_2O:lignite = 5:7was prepared.

Zirconia sol was prepared by $Zr(OC_4H_9)_4$. First, $Zr(OC_4H_9)_4$ was dissolved in 30 mL of ethanol at room temperature. Then, acetic acid was drop-by-drop added into the solution and the solution was stirred for 30 min with a magnetic stirrer. Next, ethanol-containing hydrochloric acid was added into the solution and stirred for 60 min, resulting in the formation of a transparent yellowish sol. The obtained sol was further aged at room temperature for 48 h. The ZrO_2 films were formed on the steel substrate through the spin-coating method. The coating was done at 2000 rpm for 15 s. Subsequently, the sample was sintered at 600 °C for 2 h to obtain a crystalline film. Finally, the xerogel powder was synthesized from the sol by repeating the above drying-sintering process.

2.2. Characterization of method

The crystal structures of ZrO_2 xerogels were examined by the X-ray diffraction (XRD) with a Cu Kα X-ray source operated at 40 kV and 120 mA with a 2θ/min scanning speed and the X-ray photoelectron spectroscopy (XPS) with an Al Kα(hv = 1486.6 eV) X-ray source scanning speed. The surface morphologies of the corrosion scales were observed by scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis.

3. Results and discussion

3.1. XPS analyses

XPS spectra and the corresponding peak fitting spectra are shown in Fig. 1. The Binding Energy (BE) of the elements in ZrO_2 films was well detected. The O 1 s high-resolution XPS scans are shown in Fig. 1a, which reveal peaks at a BE of 529.6 eV, corresponding to ZrO_2 [23]. Fig. 1b presents the Zr 1 s high-resolution XPS spectra of the ZrO_2 layer, in which the peaks at BE 182.2 and 184.5 eV correspond to ZrO_2 [24,25].

3.2. XRD studies

Fig. 2 shows the XRD patterns of the ZrO_2 xerogels at 600 °C, 700 °C and 800 °C for 2 h. As shown in Fig. 2, the ZrO_2 mainly consists of the tetragonal phase (t-ZrO_2) at 600 °C. When the sintering temperature rises to 700 °C, the t-ZrO_2 diffraction peak intensity is enhanced and is accompanied by a small amount of the monoclinic phase (m-ZrO_2). However, when the sintering temperature is 800 °C, the intensity of the t-ZrO_2 diffraction peaks decreases, whereas the intensity of the m-ZrO_2 peaks clearly increases. Moreover, the width of the diffraction peaks of the tetragonal and monoclinic phases are narrowed with increasing sintering temperature, indicating that the grain size of ZrO_2 increased gradually. This result can be explained by the growth kinetics of ZrO_2 crystallites.

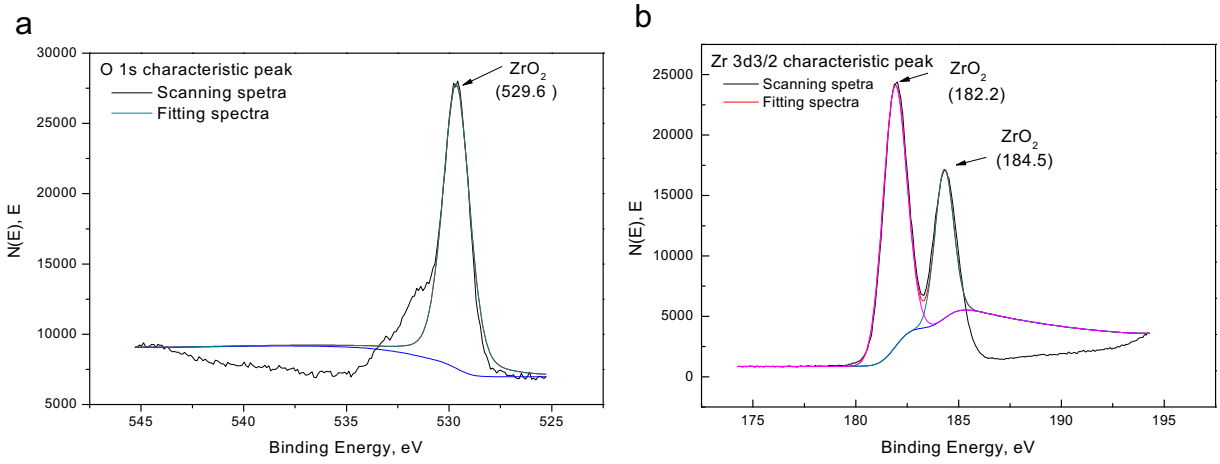

Fig. 1. XPS fitting peaks spectra of ZrO_2 layer at 600 °C: (a) O 1 s characteristic peak, (b) Zr 3d characteristic peak.