Journal of Non-Crystalline Solids 492 (2018) 18–26

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Migration and enrichment of chromium and silicon element in glass coating at high temperature

G.Y. Fu[a,b], L.Q. Wei[a,*], X.M. Zhang[a], Y.B. Cui[a], B. Yu[a,b], C.C. Lv[a,b], Y.L. Wang[a], S.F. Ye[a,*]

[a] State Key Laboratory of Multiphase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, PO Box 353, Beijing 100190, China
[b] University of Chinese Academy of Sciences, No. 19(A) Yu quan Road, Beijing 100049, China

ARTICLE INFO

Keywords:
Chromium
Silicon
Migration
Interface
Glass coating

ABSTRACT

The formation and mechanism of chromium and silicon enriched glass coating on carbon steel substrate were investigated in this paper, which was based on the protection properties of the glass coating to improve the anti-oxidation ability of carbon steel. The starting reaction temperature between the glass coating and steel substrate was 800 °C, which was approved by TG-DTA test. The diffusion of chromium and silicon element in glass coating was investigated at 800 °C and 1000 °C by WDS-EPMA and SEM-EDS. It indicated that chromium element began to migrate to interface between glass coating and carbon steel at 800 °C and a chromium enriched layer formed when the sample was heated at 800 °C for 60 min. Meanwhile, a silicon enriched layer started to form at the interface between glass coating and carbon steel at 1000 °C. The content of silicon element in the scale of coated sample increased with increasing heating time and which could reach up to 8.08% when the sample was heated at 1000 °C for 30 min. The sample was also characterized by XRD, SEM-EDS and Raman to investigate the possible phases formed during high temperature treatment.

1. Introduction

The ability of many alloys to resist oxidation was due to the continuous, slow-growing chromium scales on the surface [1–5]. Stainless steel exhibited good anti-oxidation performance due to the formation of a continuous Cr enriched α-$(Cr_xFe_{1-x})_2O_3$ scale at high temperatures [6–8]. Even if the chromium scale was destroyed, chromium element migrated to the stainless steel substrate and formed a complete oxidation protective film, which was due to the anti-oxidation performance of stainless steel. Many researchers found that stainless steel substrate had good anti-oxidation performance, which was due to the synergistic effect of glass coating and chromium trioxide film [9–12]. Therefore, chromium compounds were added into the glass coating to improve the anti-oxidation performance of carbon steel at high temperature. Experimental results confirmed that chromium element migrated to the interface between glass coating and carbon steel, and then chromium enriched layer formed at the interface between glass coating and carbon steel [13]. Meanwhile, the silicon enriched layer also formed at the interface between steel substrate and glass coating with the increasing temperature in the heating process. Hence, the chromium and silicon element were proved to be useful for preventing the oxidation at high temperature [14–18]. The property of super alloys could prevent the corrosion of silicate melt, which was directly related to the formation of chromium layer at the interface between the alloy and glass melt [19–21]. The migration of chromium element was related with the migration of silicon element [22]. The aim of this study was to found the rule of migration enrichment of chromium and silicon element in the glass coating.

In order to study on the mechanism of the migration of chromium and silicon element and the formation of a special constructions of glass coating to improve the anti-oxidation performance of carbon steel, the following work was implement in this study: the migration of chromium and silicon element was investigated; the microscopic structure at the interface between glass melt and carbon steel was also studied; the interactions between chromium, silicon elements and glass melt were investigated.

2. Experiment

2.1. Preparation of sample

Carbon steel samples were prepared in a cube shape (1 cm × 1 cm × 1 cm) by the cutting machine (High-speed WEDM). Subsequently, the samples were polished using SiC papers from 200# to 2000# grit to get a smooth surface. Then, the sample was given a complete cleaning and washing through an ultrasonic treatment and

* Corresponding authors.
E-mail addresses: lqwei@home.ipe.ac.cn (L.Q. Wei), sfye@home.ipe.ac.cn (S.F. Ye).

https://doi.org/10.1016/j.jnoncrysol.2018.03.055
Received 14 August 2017; Received in revised form 28 March 2018; Accepted 30 March 2018

Table 1
Chemical composition of carbon steel.

Component	C	Si	Mn	S	P	Fe
Content, wt%	0.24	0.37	0.65	≤0.030	≤0.030	Balance

Table 2
Chemical composition of the glass coating.

Component	SiO_2	Al_2O_3	CaO	Fe_2O_3	K_2O	Na_2O	TiO_2	Cr_2O_3
Content, wt%	68.30	9.46	0.49	3.81	3.70	6.63	0.25	6.41

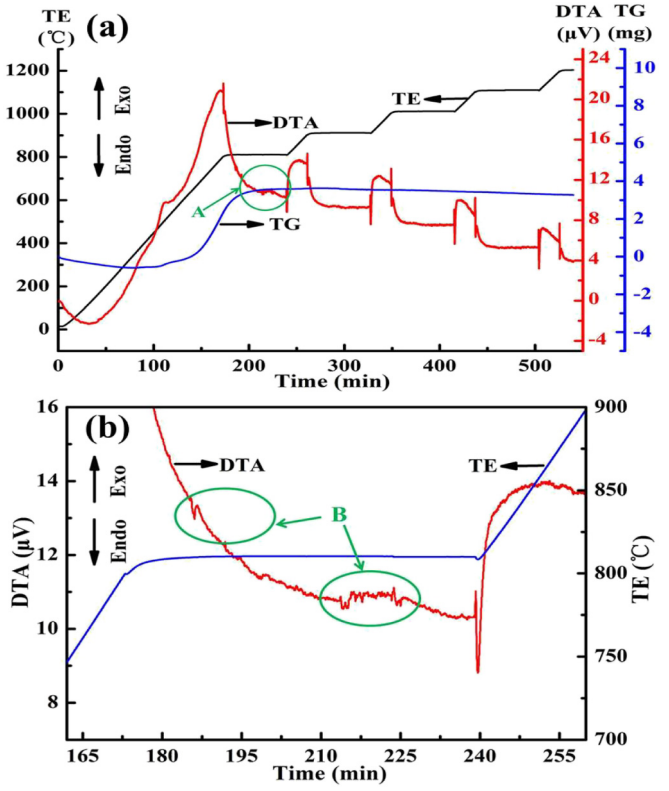

Fig. 1. TG-DTA curves of coated sample from room temperature to 1200 °C and maintained for 60 min at certain temperatures (such as 800 °C, 900 °C, 1000 °C and 1100 °C): (a) complete and (b) partial enlarged.

dried by electric drying oven for use. The chemical composition of carbon steel was shown in Table 1, which was analyzed by the direct reading spectrograph (ChemReal3764, TSI, America) and carbon and sulfur analyzer (CS-2800G, NCS Testing Technology Co., Ltd., China). The relative error of the direct reading spectrograph was less than ± 2%. Meanwhile, for the carbon and sulfur analyzer, the relative error of carbon analysis and sulfur analysis were less than ± 0.02% and ± 0.004%, respectively. The glass coating was prepared as reported in our previous paper [13]. It was consisted of the silicate, chromium oxides and sodium silicate binder. The chemical composition of the mixture was analyzed by the X-ray fluorescence (XRF; AXIOS-MAX, PANalytical B.V., Netherlands) with relative error less than ± 1%. The chemical composition of glass coating was shown in Table 2.

2.2. Evaluation of migration enrichment and characterization

The weight and energy changes with increasing temperature were detected using TG-DTA (TG-DTA; STA449, Netzsch, Germany). The structure of glass coating and the scale of coated sample were investigated by Raman Spectroscopy (Raman, invia-Reflex, Renishaw, England). The migration of chromium and silicon element was evaluated by the electron probe microanalysis (WDS-EPMA; JXA8230, JEOL, Japan). The samples was heated from room temperature to 800 °C and 1000 °C, and maintained for different times (such as 0, 10, 20, 30, 40, 50 and 60 min). Then, the sample was rapidly taken shape in 15 min by using cold inlaid materials and mold. Subsequently, the sample was polished and grinded by automatic grinding machine for microscopic observation. The microstructure of scale for coated sample was analyzed by scanning electron microscopy (SEM-EDS; JSM-6700F, JEOL, Japan). Meanwhile, the EDS spot scanning was used to analyze the chemical composition of the different microstructures under different heating treatment with relative error about ± 10%. The sample was quenched by water after high temperature treatment to obtain real-time status of sample. Then, the formed phase of the sample during heating process was analyzed by X-Ray Diffraction (XRD; X'Pert, Philips, Netherlands).

3. Results and discussion

3.1. The property of glass coating

By the weight loss and TG-DTA tests from room temperature to 1200 °C, the glass coating enhanced the anti-oxidation performance by 80% from 1000 °C to 1100 °C in the previous study [9]. It also had certified the glass coating had good anti-oxidation performance, which was due to the chromium and silicon enriched layer and mixture formed by the reactions between the glass coating and steel substrate [9]. The aim of this study was to found the rule of migration enrichment of chromium and silicon element in the glass coating. TG-DTA analysis of coated sample, as shown in Fig. 1(a), was carried out at heating of 5 °C/min from room temperature to certain temperature (such as 800 °C, 900 °C, 1000 °C and 1100 °C) and maintained for 60 min. As the carbon steel was oxidized above 650 °C by the TG-DTA test [9], the small peaks (below 650 °C) in Fig. 1(a) indicated the conversion reactions among coating materials, (such as phase transformation and melting reactions). In Fig. 1(a), there had a series of small exothermic peaks (marked as A by green circle) at 800 °C, which indicated reactions were carried out between glass coating and carbon steel at 800 °C. Fig. 1(b) was enlarged of A section in Fig. 1(a), which clearly indicated there has a series small exothermic peaks at 800 °C. Therefore, 800 °C was chosen as the reaction temperature for the reactions between glass coating and carbon steel in the following work.

The Raman spectrum, which was recorded using excitation wavelength of 528 nm, was also taken to indicate the structure of glass coating and the coated sample. Fig. 2 was Roman spectra of the glass coating and the scale of coated sample heated at 800 °C for 60 min. As shown in Fig. 2(a), there have several peaks for glass coating at 301, 348, 551 and 610 cm^{-1}. It had been approved that the peak at 301 cm^{-1} was attributed to Cr_2O_3 [23]. The peak at 348 cm^{-1} was characteristic of O-Cr-O torsion [24], and the peaks at 551 and 610 cm^{-1} were owing to Cr_2O_3 [25]. The Raman results also indicated the chromium ions mainly existed in the three valence states. It also indicated part of the chromium ion existed in the four valence states, which could clearly demonstrated the chromium ion had the reactions between the glass materials during heating treatment. Fig. 2(b) was the Raman result of coated sample. There had a series of peaks between 200 and 1000 cm^{-1}, such as 284, 343, 468, 510, 549 and 609 cm^{-1}. Compared with the Raman spectrum in Fig. 2(a), Fig. 2(b) indicated the structure of glass coating was changed by reactions between glass coating and steel substrate. The peaks at 284, 343 and 468 cm^{-1} in Fig. 2(b) were owing to Si—Si [26], O—Cr—O [23] and O—Cr—O [27], respectively. The peak at 510 cm^{-1} was owing to Fe_3O_4 [26] and the peaks at 549 and 609 cm^{-1} were owing to Cr_2O_3 [25]. The Raman results of Fig. 2 indicated new phases were formed between glass coating and steel substrate, and the states of chromium element was