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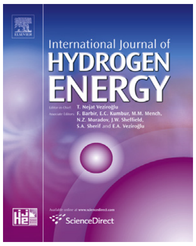

Diffusion behavior of hydrogen through thermally sprayed coating of 316L stainless steel

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ARTICLE INFO

Article history:
Received 29 September 2016
Received in revised form
2 November 2016
Accepted 3 November 2016
Available online xxx

Keywords:
Hydrogen
Permeation
Diffusion coefficient
Thermal sprayed coating
Stainless steel

ABSTRACT

Along with other hydrogen barrier coatings, thermally sprayed coating is one of the potential barriers against hydrogen permeation. In this research, specifications of hydrogen diffusion through thermally sprayed 316L stainless steel coating over structural steel are scrutinized by different methods, including complete and partial charging and discharging tests utilizing Devanathan–Stachurski cells. Besides, various mathematical methods are applied to obtain data about the diffusion coefficient of hydrogen, in addition to the solved and trapped hydrogen contents in the coating. The analyses are supported by means of X-ray diffraction (XRD) and microstructural observations to confirm interpretations of hydrogen permeation behavior across the coating. Because of the specific microstructure of the sprayed coatings and continuous ferritic phases across the coating, which develop short pathways for hydrogen diffusion, the thermal sprayed stainless steel coating exhibits diffusion coefficient near that of ferritic steels. Furthermore, the coating contains significantly more reversible and irreversible trap concentrations than that of ferritic steels comprise.

Introduction

Hydrogen has acquired many applications and significance in industries including oil and gas refining that huge amounts of hydrogen is produced and utilized in. Also, hydrogen is very noticed by nuclear industries and green energies. Waste of hydrogen by its permeation and diffusion through walls and pipes is an important problem resulting to hydrogen degradation of structures and parts, and reduction in the efficiency [1–3]. Many researches, conducted during many years to prevent hydrogen permeation and embrittlement, have resulted in proposing different preventing methods including diffusion resistant coatings [4–6]. Austenitic steels display more diffusion resistance to hydrogen than ferritic steels (>1000) [7]. As a result, they are relatively inexpensive barriers against hydrogen diffusion [7,8]. Cladded coatings of stainless steels by welding are more popular in oil and gas industry [9], but other barriers may be established along with the cladded coating [10,11] or when welding is not applicable [12,13]. One of the best and fastest coating methods is thermally sprayed coating that has many abilities to coat. Though the positive effects of thermally sprayed coating on impeding hydrogen

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http://dx.doi.org/10.1016/j.ijhydene.2016.11.026

Please cite this article in press as: Moshref-javadi M, et al., Diffusion behavior of hydrogen through thermally sprayed coating of 316L stainless steel, International Journal of Hydrogen Energy (2016), http://dx.doi.org/10.1016/j.ijhydene.2016.11.026

embrittlement of structural steels, even more than sputtered coatings [14], have been reported [15], the hindering effects of stainless steel coatings and their diffusion specifications are not evaluated yet.

Many parameters involved in the thermal sprayed coating which affect hydrogen diffusion. For example, thermal sprayed coatings always exhibit rough surface which leads to increase in permeated hydrogen per time and more hydrogen flux when the diffusion attains steady state [16,17]. Besides, surface roughness decreases the effective thickness of the membrane, resulting in shorter diffusion pathways [18]. Moreover, striking particles to the substrate in thermal sprayed coatings always produces a high level of residual stress [19–23]. Effects of residual stress on hydrogen diffusion and solution in bulk materials have been proved by many researchers [24–26]. Furthermore, many defects such as dislocations, increased by straining in the metal structure, play the role of hydrogen traps and decrease hydrogen diffusion [25,27,28]. Particles of 316L stainless steel under HVOF process are subjected to severe strain resulting in double the dislocation content for the HVOF coating [29]. Other inherent characteristics of thermal sprayed coatings are oxide layers and porosities which are effective on hydrogen diffusion and can decrease its diffusion coefficient [12,30,31]. Moreover, variation in the chemical composition of splats in thermal sprayed coatings causes alteration of diffusion specifications. Combined effects of chemical composition changes, stress, and strain can induce martensitic transformation in stainless steels coatings [32–34]. Martensitic and ferritic phases exhibit a higher hydrogen diffusion coefficient than austenite and accelerate hydrogen diffusion if construct an interconnected framework across the stainless steel membrane [33,35,36]. In addition, diffused hydrogen in austenite independently increases stress and facilitate martensitic transformations [37,38]. All of the mentioned subjects, integrated with the thermal sprayed coatings, interact with each other and are effective on hydrogen diffusion characteristics.

Consequently, the benefits of the thermal sprayed coating against hydrogen are behind of many topics to be investigated. Nevertheless, even the general behavior of hydrogen diffusion into the thermal sprayed coatings is not evaluated and understood, yet. This research is aimed at overall evaluating hydrogen diffusion specifications across the thermally sprayed coating of 316L stainless steel.

Experimental procedure

Substrates by dimensions of 3 × 300 × 300 mm were prepared from st.37 structural steel. Afterward, HVOF coating of 316L stainless steel was sprayed by parameters shown in Table 1. Specifications of the coating material are shown in Table 2. As well, XRD analysis and metallographic tests were used for phase and microstructural evaluations. Etching of the samples was performed by Braha II solution during 4 s.

Coated specimens were trimmed and thinned to the dimensions of 40 × 40 × 0.7 mm by wire cut in order to ensure one-dimensional hydrogen diffusion and decrease the duration of the permeation tests. The thickness of the specimens was measured as 701 μm and 670 μm for the substrate and the coated samples (coating with substrate), respectively. Therefore, the thickness of the coating layer for the coated specimens was 280 μm and its substrate layer thickness was 360 μm.

The substrate side of the samples was polished with 800-grade emery paper, and both sides were electrochemically coated with thin palladium layer to increase the efficiency of hydrogen reactions. In order to form palladium coatings, first, surfaces of the samples were briefly cleaned and activated in HCl 37% solution for 40 s just before immersion in the coating solution. Next, samples were washed with pure acetone and immediately put in the coating solution which was a mixture of 5 g/l of $PdCl_2$ in 28% aqueous ammonia solution. A current density of 2 mA/cm^2 for 4 min was applied on the specimens to ensure perfect covering of the Pd film on the both sides of the samples. Finally, all samples were baked at 120 °C for 3 hr under inert gas to remove entered hydrogen inside the samples during preparation procedure.

Hydrogen permeation tests for examining of hydrogen diffusion specifications through thermally sprayed coating over the substrate were performed by Devanathan–-Stachurski electrochemical cells according to ISO 17081 standard [39]. Accordingly, two cells were made of Teflon with a volume of 1 lit as charging and reducing cells. Samples with the effective area of 7 cm^2 were fastened by mechanical clamps and silicone rubber seals between the cells, facing the coated surface to the charging cell. At first, reducing cell was filled by deaerated NaOH 0.1 N solution at 25 °C, and needed time to achieve a passive current of 0.1 $\mu A/cm^2$ were established under reducing a voltage of 5 mV(Ag/AgCl). Next, while the reduction current was measured, and argon was purged to the both cells, charging cell was filled with the solution and charging with the current of 1 or 2 mA/cm^2 on the coated surface was applied. Various test methods including complete and partial hydrogen charging and discharging tests according to Zakroczymski suggestion [40] were implemented to precisely evaluate hydrogen diffusion properties. Partial hydrogen charge and discharge tests were carried out to decrease the effects of hydrogen traps on the permeation test results and to acquire bulk diffusion. On the same hand, partial tests can decrease surface effects of the specimens on the permeation results by reducing variations of hydrogen concentration at the entering surface [41]. Partial permeation tests were accomplished, while the steady state condition was established, by increasing the charging current from 1 to 2 mA/cm^2 for charging passes and vice versa for discharge

Table 1 – HVOF thermal spray parameters.

Spray distance (cm)	Gun type	Combustion chamber pressure (bar)	Oxygen to fuel ratio	Coating material	Coating passes	Oxygen flow (l/m)	Kerosene flow (l/h)
36	GTV K2	7.8	1.155	316 L	3	900	24

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