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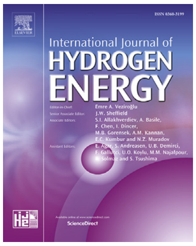

Thermal desorption spectrometer for measuring ppm concentrations of trapped hydrogen

C.V. Tapia-Bastidas [a,b], A. Atrens [c], E. MacA. Gray [a,*]

[a] Queensland Micro- and Nanotechnology Centre, Griffith University, Brisbane, 4111, Australia
[b] Escuela Superior Politécnica del Litoral, ESPOL, Faculty of Mechanical Engineering and Production Sciences, Guayaquil, Ecuador
[c] Division of Materials Engineering, The School of Mechanical and Mining Engineering, The University of Queensland, Brisbane, 4072, Australia

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ABSTRACT

This paper describes an ultra-high-vacuum thermal desorption spectrometer, designed to study hydrogen in steels at ~1 wt ppm (~50 atomic ppm) concentration. The high sensitivity achieved also facilitates the analysis of surface phenomena. The instrument was evaluated with model materials and provided good measurements of diffusible hydrogen. A hydrogen peak at ~350 °C was identified for steels exposed to water during hydrogen charging, and attributed to water molecules adsorbed on the sample surface for samples exposed to the laboratory atmosphere for times as short as 1 min. Recommendations are made for precautions to be taken when handling the samples.

Introduction

Hydrogen energy technology is seen as necessary in realising the moderate consequences scenario of an average global temperature rise below 2 °C as agreed at the United Nations Framework Convention on Climate Change meeting in Paris in 2015 [1]. There are challenges in (i) generating hydrogen using a primary energy source such as solar radiation, (ii) storing hydrogen in compact form for applications such as fuel-cell vehicles, and (iii) containment of hydrogen gas for industrial applications and energy distribution. Hydrogen influences the structure of many metallic materials, including rare-earth–transition-metal intermetallics and steels. Advantage can be taken of such changes at the microstructural scale for the storage of hydrogen in alloys and the production of high-energy-product permanent magnets from alloys that suffer decrepitation through absorbing large amounts of hydrogen [2]. At the opposite end of the concentration scale, structural alloys can be severely embrittled by ppm quantities of hydrogen. This hydrogen embrittlement can lead to the failure of an engineering component during service [3].

The distribution of gaseous hydrogen by incremental introduction into the natural gas network would be possible provided that the gaseous hydrogen does not cause hydrogen embrittlement of the pipeline steels. Similarly, it is important that the influence of hydrogen is understood for the steels used in the construction of turbogenerators for electricity

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* Corresponding author.
E-mail address: e.gray@griffith.edu.au (E.MacA. Gray).

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generation [4,5], where hydrogen cooling is used because of its high thermal conductivity. Likewise, it is important to understand the influence of hydrogen on advanced high strength steels potentially used in automotive applications [6–20]. In each of these applications, it is important to also understand the hydrogen-trap interactions [21].

As early as 1875, Johnson [22] described the detrimental effect of hydrogen in steel. Nowadays, the scientific community is still seeking a solid understanding of the hydrogen embrittlement (HE) phenomenon. HE occurs when the steel interacts with a critical amount of hydrogen, and, as a consequence, the steel mechanical properties are affected in a detrimental way: (i) as a reduction of mechanical strength, toughness and ductility, together with subcritical crack growth [23,24]; or (ii) some reduction of ductility without an appreciable decrease in yield and tensile strength, and without sub-critical crack growth [25]. HE has been thoroughly reported in different steels, including high-strength steels [8,26–29], advanced high-strength steels [14–19,30,31], and medium-strength steels [7,10,11,32].

The trapping of hydrogen in crystalline defects [33] increases the hydrogen solubility while decreasing diffusivity in the steel [34,35]. Hydrogen trapping has been linked to HE susceptibility in steels [36]. Thermal desorption spectroscopy (TDS) is a powerful technique to study hydrogen-trap interactions. TDS typically measures the amount of hydrogen desorbed from a specimen subjected to controlled heating [37–39]. TDS can be used to (i) measure low hydrogen concentrations at ~1 wt ppm, and (ii) characterise the binding energy of hydrogen traps. TDS has been useful in HE studies, is complementary to mechanical tests [37], and has been widely used to investigate hydrogen-trap interactions in steels [40–44]. For example, reversible or weak traps can act as hydrogen sources and supply diffusible hydrogen to highly stressed sites to cause HE, as reported by Thomas et al. [45] while testing ultra-high strength AERMET 100 steels via TDS. Ryu et al. [46], by performing TDS experiments, found out that austenite traps hydrogen more effectively than grain boundaries and/or dislocations in ferrite while testing transformation-induced plasticity (TRIP) steels. Conversely, the presence of well-distributed irreversible traps or strong traps would prevent HE vulnerability of the steel, especially if only a finite amount of hydrogen is available [23,47]. The hydrogen trapping effect caused by the inclusion of different elements, such as titanium [29,43,48–51], niobium [52–55] or vanadium [56,57] has been studied thoroughly in order to get an in-depth understanding of the possible beneficial effect of having strong traps – linked to the carbides formed-to capture the hydrogen intake in service.

This paper describes a thermal desorption spectrometer (TDS) that has been built to accurately characterise the evolution of hydrogen in steels at concentrations of 1 wt ppm. This concentration is around 100 times lower than the detection limit of Sieverts or gravimetric apparatus used to study hydrogen storage materials. This TDS instrument is able to provide a direct, precise and selective measurement of the kinetics of the hydrogen desorption from the steel when the hydrogen-charged steel sample is heated at a constant rate.

The TDS is an improved version of the ultra-high-vacuum (UHV) TDS [39,58] design of Smith and Scully [59], used to investigate hydrogen embrittlement of Al-Li-Cu-Zr alloys, hydrogen-trapping in experimental steels [43,60], and hydrogen trapping and hydrogen embrittlement of ultra-high strength steels [61–63].

The basis of the UHV-TDS technique is controlled desorption of hydrogen from the sample under ultra-high vacuum (UHV) conditions, which minimises the background of hydrogen and other species that ultimately sets a lower detection limit. The flow of hydrogen released from the sample to a throttled vacuum pump establishes a hydrogen pressure proportional to the hydrogen molar flow rate, and allows measurement of low hydrogen concentrations. The hydrogen desorption spectrum measured during a controlled temperature ramp allows evaluation of trapping parameters using the Kissinger model [64], to associate the hydrogen desorption peaks with the activation energies of particular hydrogen traps.

The approach of measuring hydrogen evolution during a temperature ramp is familiar in research into solid-state hydrogen storage, where temperature programmed desorption is applied to characterise the desorption kinetics. The process is the same in principle, but the higher hydrogen concentrations in the case of hydrogen storage materials allow the use of a vacuum gauge to detect the evolved hydrogen.

The TDS technique uses a mass spectrometer to analyse and quantify the flow of species in the analysis chamber. This means that hydrogen can be detected against a significant background of other species, and also the total amount of hydrogen in the sample can be measured at the ppm level. Furthermore, simultaneous calibration for other species allows study of reactions on the sample surface.

The high sensitivity achievable with UHV-TDS has recently been applied by Silvestri et al. [58] to study the surface-contamination of iridium standards for mass metrology. A key development was to integrate inert-atmosphere handing of the sample to exclude adventitious surface water.

This paper describes the new instrument. Some illustrative results are provided for well-known materials, including (i) standard calibration samples normally used with the hot extraction technique [65] for quantifying total hydrogen content, (ii) commercial low-carbon steel containing diffusible hydrogen, and (iii) palladium containing trapped hydrogen. A study is presented of the interfering effects of adventitious adsorbed surface water showing that, at the ppm level, inert-atmosphere handling would be advantageous for measuring the desorption of hydrogen absorbed into the interior of the sample.

TDS theory

Measurement of amount of species

The theory of the analysis using TDS and related techniques has been reviewed [66–70]. Our focus is on (i) the measurement of the thermal desorption spectrum, and (ii) the

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