



Influence of experimental parameters on thermal desorption spectroscopy measurements during evaluation of hydrogen trapping



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ABSTRACT

Thermal desorption spectroscopy (TDS) was performed on two steels, (i) S550MC (an industrial, micro-alloyed high strength low alloy steel), and (ii) C075, a lab cast TiC containing steel. The influence of experimental parameters was studied which were related to hydrogen charging, sample features and the TDS measurement itself. It was found that the experimental conditions can significantly influence the TDS results. The results indicated that all experimental parameters are important in hydrogen related research and a reproducible experimental procedure is important in order to guarantee a reproducible analysis of the hydrogen trapping behavior by means of thermal desorption spectroscopy.

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1. Introduction

Hydrogen in steels may decrease ductility, and may allow unpredictable fracture, at a lower fracture stress than in air. Sensitivity to hydrogen embrittlement increases with increasing steel strength, although there is considerable debate as to the reason. This arises as a consequence of the complex nature of the hydrogen interaction with the steel. Issues include hydrogen solubility, possible hydride formation, hydrogen mobility, impact of hydrogen on the phase stability in the steel microstructure, the interaction of hydrogen with the stressed lattice, and the interaction between hydrogen and microstructure defects [1]. The manner of how hydrogen behaves inside the steel is of crucial importance.

Various methods are used to study hydrogen absorption and trapping. Degassing of pre-charged steel immersed under mercury at room temperature can measure the volume of hydrogen in the crystal lattice and in reversible traps. This technique is confined to steels with sufficiently high hydrogen diffusivity, such as low alloy carbon steels. Hot extraction at elevated temperatures measures the total hydrogen content, including in all types of sites, including irreversible traps. These methods give no information on the binding energy of traps.

The electrochemical hydrogen permeation method, developed by Devanathan and Stachurski [2], can measure the hydrogen solubility for each charging condition, the density of traps, and the binding energy of the dominant reversible trap. Repeated

permeation transients allow study of irreversible and reversible traps. However, resolution of the different types of irreversible traps is usually not feasible, and is difficult even when using a number of specimens with systematically varying metallurgical treatments [3].

Thermal desorption spectroscopy (TDS) can provide, from one measurement, all the required information about hydrogen, including the density and binding energy of each of a series of traps. Furthermore, TDS can be used with steels with a small hydrogen diffusion coefficient, for which the test duration is long with the other techniques [4]. TDS experiments classify hydrogen traps into strong and weak traps.

TDS [5–9] was originally developed as a surface science technique to study adsorption and desorption kinetics of adsorbed layers, to define binding states of adsorbates, and the thermal evolution of adsorbate layers.

TDS is used in steel research as a non-isothermal technique, to study hydrogen desorption, and hydrogen distribution within traps. TDS uses pre-charged samples. The pre-charged sample is typically subjected to a linearly increasing temperature. The amount of desorbed hydrogen is measured by a mass spectrometer, e.g., a quadrupole mass spectrometer, tuned to the mass-to-charge ratio of ionized hydrogen. Some TDS apparatus have used a carrier gas (e.g., N₂ or He) to transport the degassing hydrogen to the mass spectrometer. The most common TDS uses ultra high vacuum. For these, it is necessary to reach an appropriate high vacuum before starting the test. During this time, hydrogen diffuses out from the specimen, which is a disadvantage.

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TDS is mechanically non-destructive, but annealing might change the microstructural features. Indeed, many hydrogen traps are not changed by the thermal treatment, but this is not always the case. For example, Nagumo et al. [10] demonstrated that the TDS temperature ramp caused the recovery of the deformed microstructure for pure iron, interstitial free steel, and eutectoid steel. The hydrogen desorption was accompanied by the annihilation of the traps. Pérez Escobar et al. [11] showed that the hydrogen released from retained austenite at $\sim 450^\circ\text{C}$ was accompanied by the decomposition of the retained austenite, as was confirmed by differential scanning calorimetry and scanning electron microscopy. Nevertheless TDS analysis often assumes that the thermal desorption takes place from trap sites which themselves remain stable during heating.

Hydrogen is mobile as demonstrated by Duprez et al. [12]. They found almost complete recovery of tensile ductility one week after cathodic hydrogen charging of a transformation induced plasticity (TRIP) steel. This indicated that the ductility loss immediately after hydrogen charging was caused by diffusible or weakly trapped hydrogen, and that immediately after charging, diffusible hydrogen started to effuse, as was also found by Pérez Escobar et al. [13]. Aoki et al. [14] defined diffusible hydrogen as hydrogen desorbed between room temperature and 500 K, during a TDS measurement, and maintained that this hydrogen effuses from the steel at room temperature in a few days after hydrogen charging.

Irreversible damage can be induced by the cathodic hydrogen charging, when the charging is carried out at high current densities for long charging times, i.e., for several days.

Surface effects may also play a role. Wei and Tsuzaki [15] argued that compounds formed at the sample surface might hinder low temperature hydrogen desorption. Retardation of desorption at low temperatures, and a steeper desorption peak, occurred after they removed the sample from the ultra high vacuum desorption chamber, cleaned the sample with acetone, and placed the sample back in the desorption chamber within 5 min.

Absorbed hydrogen is not homogeneously distributed. Hydrogen in normal lattice sites is diffusible hydrogen, and spontaneously desorbs from the sample. The remaining hydrogen is segregated to atomic and microstructure imperfections, such as vacancies, solute atoms, dislocations, grain boundaries, voids and second phase particles. In these localized regions, the mean residence time of a hydrogen atom is considerably longer than in a normal interstitial lattice site. Each of these sites is characterized by a binding energy E_B that needs to be supplied for the hydrogen to be released from the trap. If the binding energy, E_B is small, the trap is reversible. A reversible trap can act as either a hydrogen sink, which captures hydrogen atoms from weaker traps, or as a hydrogen source, which provides hydrogen atoms to stronger traps. A large E_B indicates an irreversible trap, which normally, does not release hydrogen. The binding energy of 60 kJ/mol H for

Table 1
Electrochemical hydrogen charging conditions for steels; RT = room temperature [12,26–41].

Sample preparation	Electrolyte	Current density (mA/cm ²)	Charging time	Temp. (°C)	Post-charging treatment	Ref.
–	3% NaCl + 0.3% NH ₄ SCN or 0.1 M NaOH	Variable to control H-content	48 or 72 h	RT	Cd plating	[26]
–	0.5 g As ₂ O ₃ –0.25 g HgCl ₂ –60 ml H ₂ SO ₄ /1 L H ₂ O	0.8	5 min to 4 h	RT	–	[12]
Mechanical polished with emery paper to 2500 grit	1 N H ₂ SO ₄ with 20 mg/L thiourea	Less than a few mA/cm ²	2 h	50 °C and RT	–	[27]
–	pH 2.5 H ₂ SO ₄ solution with 0.09 mass% NH ₄ SCN	5	–	30 °C	–	[28]
–	3 Mass% NaCl + 0.3 mass% NH ₄ SCN	0.1	1 h	–	–	[29]
–	0.5 g As ₂ O ₃ –0.25 g HgCl ₂ –60 ml H ₂ SO ₄ /1 L H ₂ O	0.8	1 h	RT	Washed with distilled water and acetone, polished to remove electrolyte & cleaning	[30]
–	3% NaCl solution with NH ₄ SCN	0.1	1 h	RT	Dipped into liquid N ₂ to prevent H escape	[31]
Mechanically polished with abrasive paper, electropolished, etched with 3% nital	4.8% H ₂ SO ₄ with 0.14% H ₂ NCSNH ₂	10 (ultra low carbon steel)	120 min (ULC)	–	–	[32]
		–20 (tempered martensite)	–240 min (temp mart)			
Polished with emery paper, electropolished in 860 ml H ₃ PO ₄ + 100 g CrO ₃	1 N H ₂ SO ₄ +5 mg/L NaAsO ₂	50	1–24 h	RT	–	[33]
–	1 N H ₂ SO ₄	5	6 h and 48 h	25 °C	–	[34]
–	1 N HCl	1 and 5	24 h	–	–	[35]
–	1 N H ₂ SO ₄	5	24 h	22 ± 2 °C	–	[36]
–	0.05 M H ₂ SO ₄ with 4 mg/L selenious acid	5	1 h	–	–	[37]
–	3% NaCl with 3 g/L NH ₄ SCN	0.5	–	RT	–	[38]
	4% H ₂ SO ₄	3	5 min	–	Cd plating, baking 0.5–3 h in air at 150 °C	[39]
	H ₂ SO ₄ –H ₂ O–CH ₃ OH–NaAsO ₂ –solution	6	Variable	–	–	[40]
–	5% H ₂ SO ₄ in ‘Poison P’ (20 mg/L)	80	3 h	20 °C	–	[41]

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