

Quantitative determination of hydrogen in solids by gas chromatography

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Abstract

Processes such as electroplating or acid cleaning are notorious causes of post-processing failure through hydrogen embrittlement. So, the determination of amounts of hydrogen in metals is of great importance. An analysis method for investigation of H content in solids has been established based on hot extraction and gas chromatography system. Hot extraction in inert gas enables complete and/or partial removal of the hydrogen from the samples. A gas chromatography system is used to determine quantitatively the amount of thermally desorbed hydrogen. An investigation of the baking operating conditions is made of the hydrogen desorption rate of zinc-plated steel parts. Then, an analysis of the polarisation conditions upon chromium electroplating is given.

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1. Introduction

Hydrogen can be introduced into metals during the making process, fabrication or service [1,2]. Thus, surface treatments in aqueous solutions can generate hydrogen at the surface of the parts. Electroplating processes generally have a current efficiency of less than 100% and a proportion of the current passed during electrodeposition results in the generation of hydrogen. In addition, these can include such processes as acid cleaning or cathodic degreasing. Most of the hydrogen atoms thus formed quickly combine to form diatomic gaseous hydrogen but a portion of it enters the metal and remains as individual atoms “in solution” [3]. If sufficient hydrogen is absorbed in these processes, it leads to hydrogen embrittlement with consequent damage, especially when high strength steels are electroplated [4]. So, the determination of hydrogen occluded in metals is of prime importance to the safe use of the materials and the control of the processes presented major challenges to the electroplaters. Thus, the extraction of hydrogen occluded in metals

has undergone extensive development in the last 30 years, and several review articles of this subject have published [5,6]. Numerous techniques have been used to investigate the amount of hydrogen. Conventional techniques (hot extraction, vacuum fusion, inert gas fusion, thermal desorption spectroscopy) with resulting gas mixture analysed with optical spectrograph or mass spectrometer, are in competition with differential scanning calorimetry, electrochemical and NMR methods [7–14]. The authors have chosen to develop a gas-carrier method that may be used in routine analysis. The method advanced here has been inspired by that of Brulé et al. [15] for the determination of hydrogen content in steels.

The aim of this study was to develop an analytical procedure to determination of hydrogen thermally desorbed from metals. This work fell in two stages. In a first step, we presented the outline of the apparatus: hot extraction coupled with gas chromatography analysis. Then, we applied with technique to determine the thermal desorption kinetics of hydrogen occluded in electroplated parts (zinc- and chromium-plated steels specimens).

In this paper, we present results for the detection of hydrogen desorption from electroplating parts. The measurements

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were accomplished in a new experimental system composed of a gas chromatograph connected to a thermal desorption system.

2. Experimental

2.1. Sample preparation

To carry out this investigation, we used two different types of samples: chromium-coated and zinc-coated steel parts.

- (i) Samples were of low-alloyed steel (type 38Cr4; 0.37% C, 0.18% Si, 0.81% Mn, 0.018% P, 0.007% S and 1.00% Cr) in the form of discs (chromium plating) or cylinders (zinc plating). Electroplating was performed on the steel surfaces after pre-treatments included hot alkaline soak cleaning, electrolytic cleaning and acid pickling. Because of considerable amount of hydrogen might be introduced during surface preparation, baking to remove it followed these operations. Prior electroplating, acid dip to re-activate the surface was necessary, with an immersion time minimised (30 s).
- (ii) Zinc and chromium platings were performed in the following solutions:
 - (a) Zinc plating was carried out on cylinders 6 mm diameter and 15 mm long in the low-cyanide electrolyte containing 25 g L^{-1} NaCN, 80 g L^{-1} NaOH and 12.5 g L^{-1} Zn. The electrolyte was similar to that used commercially, except that no brighteners were added. The plating lab barrel was an $110 \text{ mm} \times 60 \text{ mm}$ horizontal cylinder with 1-mm² holes. It was equipped with a flexible dangler contact to carry the current ($J = 1 \text{ A dm}^{-2}$). Its rotational speed was kept constant at 8 rpm. High-grade zinc anodes were used. The thickness of the deposit was equal to 10 μm for all experiments.
 - (b) Chromium coatings were obtained on discs (13 mm diameter and 3 mm thick) in a lab rack plating plant from a hexavalent chromic acid electrolyte corresponded to the one of most commonly used in industry. It was composed of 250 g L^{-1} of chromium trioxide and 3 g L^{-1} of sulphuric acid. Thermal regulation was necessary to keep the temperature of the plating solution constant at $50 \pm 0.5 \text{ }^\circ\text{C}$. Sb7–Pb93 alloy sheets were used as anode for electrolysis.

Tests were carried out to investigate the influence of the polarisation [16–18]. Two types of polarisations were studied: (DC) direct current polarisation ($J = 40 \text{ A dm}^{-2}$) and (RPC) reversal pulsed current polarisation (Table 1). The pulse plating parameters were being illustrated in Fig. 1. The quantity of charge used for electrolysis was fixed for all the experiments at $144 \times 10^3 \text{ A s dm}^{-2}$.

Table 1
Plating conditions

	J_c (A dm^{-2})	T_c (ms)	J_a (A dm^{-2})	T_a (ms)	H_2 (ppm)
DC	40	–	–	–	12
RPC	48	13,000	48	40	21

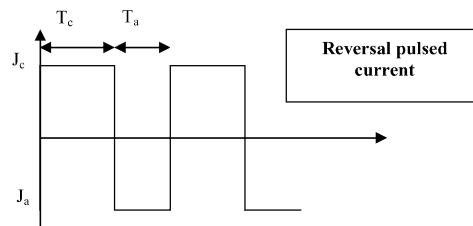


Fig. 1. Reversal pulsed wave. T_c : cathodic time pulse length, J_c cathodic pulse current density, T_a : reverse on time or anodic pulse length and J_a anodic pulse current density.

2.2. Analysis apparatus and procedures

A gas chromatography system was developed for determination of hydrogen content in solids, thermally desorbed. The hydrogen desorption kinetic was measured using a Perkin-Elmer Autosystem XL gas chromatograph which is shown schematically in Figs. 2 and 3. The chromatograph was equipped with a $2 \text{ m} \times 1/8 \text{ in.}$ (1 in. = 2.54 cm) stainless steel column packed with molecular sieve (80–100 mesh, SAE 30 phase), a rotary multiway valve for change flow paths and a thermal conductivity detection (TCD) system. This column kind is necessary to have better resolution in analysis, because it was used since long time for the analysis of gas in air. The TCD used, gives better precision and the repeatability is ensured by the number of the tests to carry out. The pressure was equal to 1.2 bars and the furnace temperature was $65 \text{ }^\circ\text{C}$. The carrier gas (argon U) flow rate was 7 mL/min . The temperature of the detector block (TDC) was $100 \text{ }^\circ\text{C}$.

In an external cell, the samples were heated under inert gas from room temperature to the wanted temperature

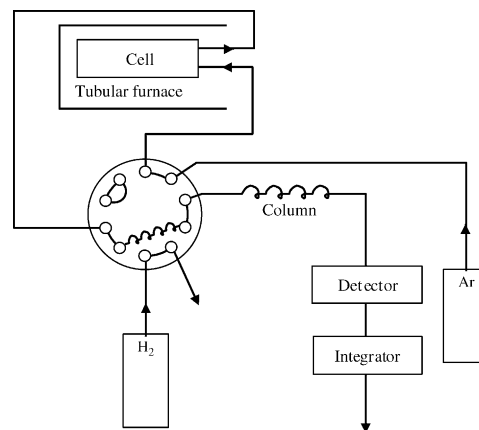


Fig. 2. Experimental setup for gas chromatography measurements (injection position).

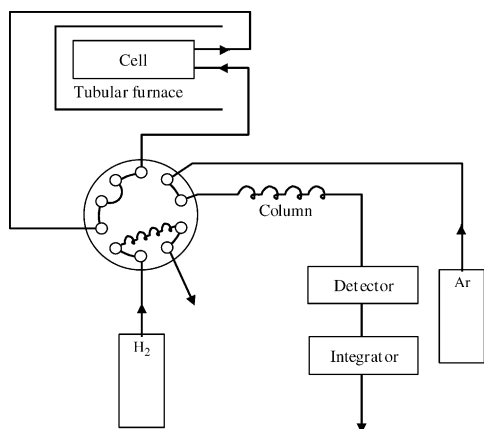


Fig. 3. Experimental setup for gas chromatography measurements (standby position).

with a variable heating rate using a furnace. Silica was used as the material cell in consideration of the permeability of hydrogen and for its resistance to hot temperatures, despite its brittleness. The size of the cell (volume 175 mL, diameter 3 cm) was such that industrial small parts can be contained. The furnace temperature (Gero Hochtemperaturofen, Neuhausen, Germany) was measured accurately and kept constant.

2.3. Procedure

(1) Calibration

In order to obtain relationship between the volumes of hydrogen released from the samples and the area of the peak, measurements were repeated by using H₂ gas with four different volumes of calibration loops (Figs. 2 and 3). At first, cell, loop and column were purged with Ar carrier gas in injection position. Then, volume of hydrogen gas was filled loop in standby position, and finally, this amount of hydrogen was detected in injection position.

(2) Sample measurements

For each measurement, the sample studied was put into the cell in which the air was displaced by argon gas and the H₂ gas stream was off (injection position). After a predetermined time, the sample was heated at an elevated constant temperature (standby position). The released diffusible hydrogen was injected with the carrier gas from the cell to the analytical section and assayed (injection position). The hydrogen was detected by the gas chromatograph of the TCD system and an integrator determined the amount of hydrogen in the carrier gas (Fig. 4). The same retention time (4 min) for hydrogen calibration and hydrogen providing of sample, prove that hydrogen detected is H₂ molecular. The hydrogen content can be calculated from a calibration curve (Fig. 5).

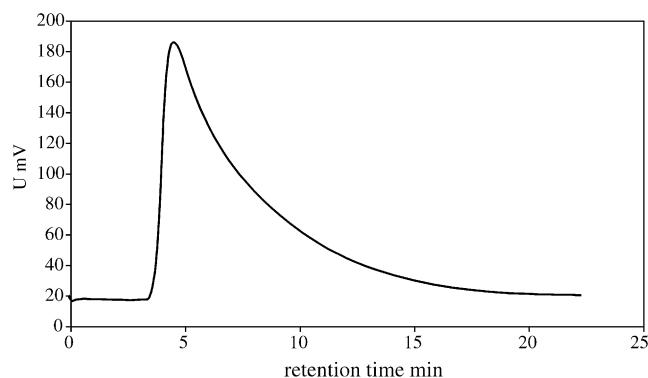


Fig. 4. Typical chart record.

3. Results and discussion

3.1. Calibration of the system

In order to determine the absolute value of desorbed hydrogen, it was necessary to accomplish a proper calibration of the system, i.e. to obtain relationship between the volumes of hydrogen released from the samples and the area of the peak. A calibration with U-hydrogen gas (99.995% purity) was used. Hydrogen gas samples, ranging in volume from 50 to 5000 μ L, were injected using definite calibration loops. The results of this calibration can be seen in Fig. 5.

3.2. Influence of the extraction temperature

When hydrogen embrittlement is thought to be a risk a de-embrittlement treatment may be required. Following zinc plating, for example, steels are baked for 8 h at a temperature in the range 190–230 °C.

Fig. 6 shows the experimental results of a 200 °C baking analysis for a zinc-coated steel. The curve was an average of three runs. Starting from zero time, the observed curve showed a time lag, at the start, owing mainly to the time required for the specimens to attain the temperature

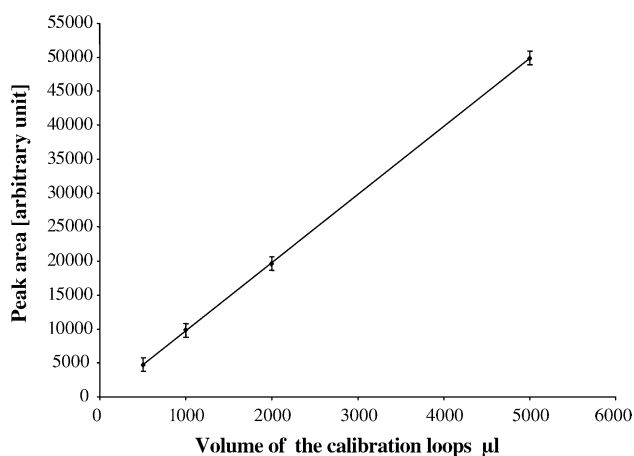


Fig. 5. Calibration curve.

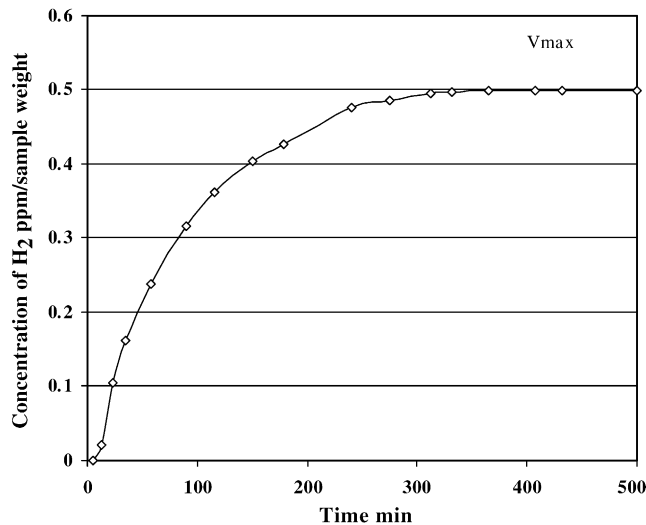


Fig. 6. Typical concentration of hydrogen evolution curve.

of the furnace. The volume of H_2 increased gradually after this time lag and finally became stationary (V_{max}). V_{max} represented the maximum volume of hydrogen thermally extracted from the specimens at the considered temperature. Fig. 7 showed the hydrogen evolution at various constant temperatures for zinc-coated steels from the cyanide bath under identical conditions. At 200 °C, the hydrogen content increased only slowly with time. By raising the extraction temperature, the hydrogen evolved changed more rapidly, so that at 350 °C the hydrogen evolution has come to an end after 15 min, while at 300 °C it took 50 min for all the hydrogen to be given off the sample. At an extraction temperature of 220 °C, the hydrogen evolution was still not complete after 150 min. In spite of the great difference in the quantity of the evolved hydrogen caused by the difference in temperature, the general trend of gas evolution was quite similar. As may be seen from Fig. 7, there was no evolution of hydrogen

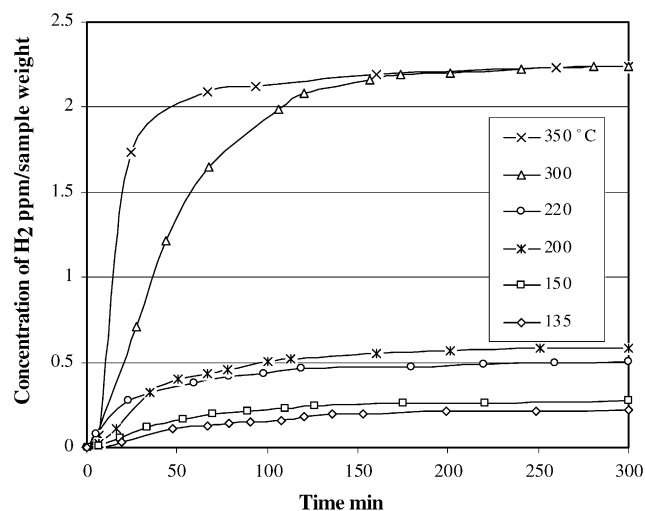


Fig. 7. Hydrogen evolution from zinc-coated steel specimens during hot extraction at various constant temperatures.

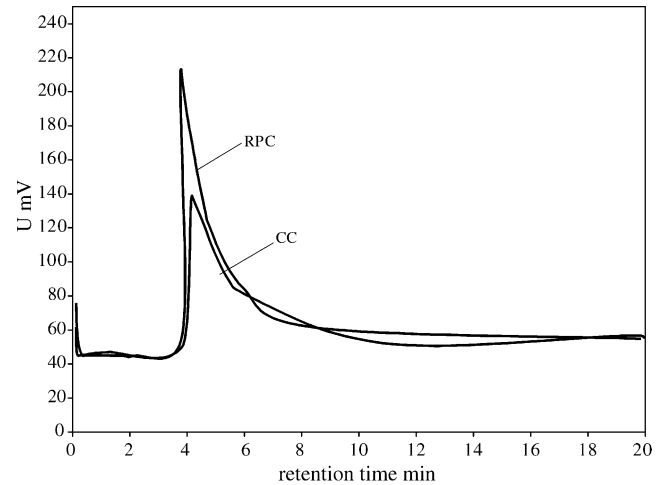


Fig. 8. Typical chart record: for direct current polarisation (DC) and reversal pulsed current polarisation (RPC).

below 135–150 °C. Hydrogen evolution first became evident above this temperature. With rising temperature, the rate of hydrogen evolution increased. In addition for chromium: the results show that the operating conditions of electrolysis have a great influence on the quantity of hydrogen occluded in the deposits (Fig. 8).

4. Conclusion

Even if numerous techniques can be used to determine hydrogen in metals (e.g., vacuum techniques, electrochemical techniques), the carrier-gas methods of collecting hydrogen is adapted to both fusion and hot extraction. The technique developed by the authors involves heating the samples to between 50 and 1000 °C (temperatures far lower than the fusion temperature of steel) and passing the gas into a gas-chromatograph column. The advantage of this method is the ease with which the kinetics of hydrogen evolution as a function of temperature can be followed and the quite sensibility of the detection of hydrogen by thermal conductivity, making it possible to detect 0.1 ppm of hydrogen. The simplicity and the non-destructiveness of the method permit the use of this apparatus in routine analysis.

The future study will include an investigation of the amount of non-occludable hydrogen as a function of the metallurgical microstructures of the parts and of operating plating conditions, some explanations about the desorption mechanisms, a contribution to the improved metals susceptibility to store hydrogen and the influence of metallurgical variables (composition, microstructures).

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