

# Thermal Analysis on Hydrogen Charged Annealed and Hardened AISI 420 Stainless Steel

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## Abstract

*After a hydrogen cathodic charging at constant current density AISI 420 stainless steel with annealed and quenched structure are analysed with the thermal analysis method.*

*The degased hydrogen quantity at three temperature ranges, till 800 °C are considered.*

*The selected charging times are in the range 30 min and 3000 min; the break periods after charging are 20 min and 1440 min.*

*The plot of total degased hydrogen versus charging time is no monotone and has a maximum for 1000' of charging for quenched and annealed steel.*

*The fraction of extracted hydrogen in the range at highest temperatures decreases until 1000 min of charging and then it remains about constant.*

*Semi-quantitative evaluation of phenomenology is suggested considering the higher diffusivity of annealed structure compared with quenched one.*

## Riassunto

È stato analizzato mediante la tecnica dell'analisi termica l'acciaio inossidabile AISI 420, considerato nella duplice condizione strutturale di solubilizzato e di temprato, successivamente ad un caricamento catodico con densità di corrente costante.

Sono state considerate le quantità di idrogeno degasato entro la temperatura di 800°C. Le condizioni di caricamento hanno previsto tempi di caricamento elettrolitico compresi tra 30 e 3000 min, con intervalli di attesa precedenti l'analisi termica di 20 e 1440 min.

Le curve relative della quantità d'idrogeno degasato in funzione del tempo di caricamento, presentano un andamento non monotono, mostrando un massimo in corrispondenza al caricamento di 1000 min, sia nel caso dell'acciaio provato nella condizione strutturale di solubilizzato che di temprato.

La frazione d'idrogeno estratto nell'intervallo di temperatura più elevato, si riduce in corrispondenza al tempo di caricamento di 1000 min, per poi rimanere tendenzialmente costante.

Comparando la più elevata diffusività della struttura solubilizzata con quella della struttura temprata, viene proposta una valutazione semi-quantitativa del fenomeno.

## Introduction

Hydrogen, interacting with some metals and alloys, in particular steels reduces mechanical properties with different damage levels.

During cathodic charging the absorbed hydrogen gives localized concentration at suitable dis-homogeneities such as grain boundaries, second phase particles and tangled dislocations.

The role of hydrogen in the embrittlement has been studied considering the types and amounts of lattice defects acting as trapping sites of hydrogen in steels with bcc and fcc structures during cathodic charging.

Trapping parameters such as the trap activation energy ( $E_{at}$ ), trap binding energy ( $E_b$ ) and trap density for each trap have been examined by using some different experimental techniques such as permeation measurements [1], autoradiography [2] and hydrogen thermal analysis methods [3-4].

In the present paper the characteristics of hydrogen evolution from the specimens are examined by carrying out the thermal analysis after the cathodic charging.

With the assumption that the escaping reaction of hydrogen from a trap site such as Fig. 1 is a thermally activated process, the hydrogen evolution rate from a trapping site can be written as

$$\frac{dX_T}{dt} = A(1 - X_T) \exp(-E_{aT}/RT) \quad (1)$$

where  $X_T = (N_0 - N)/N_0$ ,  $N_0$  is the amount of hydrogen in a trapping site at  $t=0$ ,  $N$  is the amount of hydrogen in a trapping site at  $t \neq 0$ ,  $A$  is the reaction constant,  $R$  is the gas constant and  $T$  is the absolute temperature. The term  $1 - X_T$  in (1) expresses the amount of hydrogen remaining at the trapping site and  $\exp(-E_{aT}/RT)$  represents the probability that hydrogen escapes from the trap site to the normal lattice site. Therefore, in a bcc structure, where the lattice diffusion of hydrogen is fast enough, it is assumed

that the overall hydrogen evolution reaction is controlled by the detrapping process from a trap site to a normal interstitial lattice site.

When the hydrogen charged specimen is heated with a uniform heating rate  $\Phi$ , the hydrogen evolution rate peak is formed at a certain temperature related to the trap activation energy of each trap site. At the maximum hydrogen evolution rate, the first derivative of equation (1) is zero, and so the following equation may be derived:

$$\frac{E_{aT} \Phi}{RT^2} = A \exp(-E_{aT}/RT_c) \quad (2)$$

Taking logarithms of both side of (2) and differentiating with respect to  $1/T_c$  yields

$$\frac{\partial (\ln \Phi T_c^2)}{\partial (1/T_c)} = \frac{-E_{aT}}{R}$$

The trap activation energy  $E_{aT}$ , needed to escape from the trap site to the normal lattice site, may be calculated from the slope of a  $\ln(\Phi T_c^2)$  versus  $1/T_c$  plot by measuring the charged in peak temperature with the heating rate. However, when the activation energy for lattice diffusion is very large relative to the trap activation energy, diffusion-controlled hydrogen evolution will be measured.

Thus, a hydrogen evolution rate peak related to bulk diffusion appears. Therefore, in hydrogen thermal analysis experiments, the character of the hydrogen evolution rate peak is determined by the rate-controlling step in the overall evolution reaction.

The trap binding energy  $E_b$  between the trap site and hydrogen is obtained from the relation between the hydrogen-charging temperature and the amount of hydrogen trapped at the trap site, with the model of McNabb and Foster [5].

## Methods and materials

Specimens were hydrogen charged in galvanostatic control in the apparatus shown in Fig. 2. In order to put the attention on the parameters of charging of the hydrogen cathodically, ARMCO iron specimens, cutted from bar of 10 mm diameter, were previously used. The specimens, with a cylinder shape ( $D = 5$  mm,  $h = 20$  mm), were surface finished with wet SiC paper n. 600, then rinsed in alcohol in ultrasonic apparatus.

Cathodic charging was performed at room temperature in a 0.1 N sulphuric acid solution; the applied current density was varied from 4 to 20 mA/cm<sup>2</sup>.

The times of charging were 30', 100', 500', 1000', 3000' and the break periods after charging were 20' or 1440' (24 h).

No external stress was applied during cathodic charging.

The cathodically charged specimen was cleaned by alcohol and dried then termically analysed after a period of break of 20' or 1440' (24 h).

During this period the specimen was put into a desiccator to remove the mobile hydrogen, in part or totally, so that only trapped hydrogen remained in the specimen. The thermal analysis of hydrogen was conducted by the furnace LECO HW 200.

The detection method of the analysis furnace is a thermal conductivity cell that has the ability to detect the difference in the thermal conductivity of gases. The cell consists of two pairs of matched filaments used in four legs of a Wheatstone bridge. Once the bridge is balanced and stabilized under proper conditions, the only variations in bridge output will be due to variations in the type and quantity of gas present at the measure filaments. The bridge is balanced with nitrogen flowing in both the measure

chamber and the reference chamber. The introduction of hydrogen will cause the temperature of the measure filament to decrease because hydrogen has a higher thermal conductivity than nitrogen. The sensitivity of system ( $\pm 2\%$  of the answer) is governed by the bridge current and the difference in thermal conductivity between the analyzed gas, hydrogen, and the carrier gas, nitrogen.

The specimen was heated without a uniform rate, but with a settled trend presents in Tab. 1. This settled trend was established considering the traps classification as a function of trap activation temperature.

The experience on isothermal analysis of hydrogen degassing and classification of trap sites of Asaoka [6] were considered also for break time after charging of 0.3 h, just to appreciate different types of trapping. After some methodological experiences on ARMCO iron, was tested AISI 420 stainless steel, considered with two different structures: martensitic and ferritic-perlitic.

Considering the tests with 2, 4, 6, 8, 10, 12, 14, 20 mA/cm<sup>2</sup>, the hydrogen degased quantity in ARMCO iron showed the scatter of results. Reproducibility falls at higher "current densities". At smaller current was not possible to obtain a significant difference among the various charging time. 8 mA/cm<sup>2</sup> was considered the best choice and this was the preferred current density for the tests on AISI 420 steel.

The temperature during charging was 25 °C and the solution was the same used for ARMCO iron, without a recombination poison agent. For the thermal analysis was decided to use the same settled trend choosed for ARMCO iron.

The detection furnace printed the results showing a diagram of extracted hydrogen from steel, measured in ml/100 g, as a function of temperature.

The chemical compositions of ARMCO iron and AISI 420 are given in Tab. 2.

ARMCO iron was used after a thermal treatment of 1 hour at 600 °C.

AISI 420 involved austenitising at 950 °C for 30' in an argon furnace, followed by furnace cooling to obtain a full annealing structure or oil quench to obtain a martensitic structure.

## Results and discussion

The ARMCO specimens were cathodic charged, for different periods, using various current densities (Fig. 3).

**TABLE 1 - Function Time-Temperature of Thermal Analysis**

|         | Temperature<br>(°C) | Time<br>(s) | Rate<br>(°C/min) |
|---------|---------------------|-------------|------------------|
| Range A | 50-400              | 300         | 200              |
| Range B | 400-600             | 300         | 200              |
| Range C | 600-800             | 600         | 200              |

**TABLE 2 - Chemical composition of materials (wt %)**

|          | C    | Cr   | Mn     | Si   | S    | P    | Ni   | Fe   |
|----------|------|------|--------|------|------|------|------|------|
| AISI 420 | 0.16 | 12.4 | 1.02   | 0.25 | 0.03 | 0.04 | 0.54 | rest |
| Fe ARMCO | 78   | -    | tracks | 0.19 | 0.05 | 0.03 | -    | rest |

Specimens were hydrogenated for different periods of time but over long charging periods the reproducibility was poor [7].

As some other authors referred, after the initial increase in hydrogen content a slight decrease of it was found during short charging periods (about four hours), at current density of the order of 0.05 - 0.5 mA/cm<sup>2</sup> [8], but this is not the present condition.

In previous works a similar phenomenon of decrease of hydrogen content during long charging period was observed by one of the authors [9] for a steel of grade AISI 420 full annealed with the method of pre-aged fracture, proposed by Hyspecka and Mazanec [10]. For times of charge the progressive penetration of hydrogen first causes a fall of toughness, expressed in per cent of reduction in area (Fig. 4), afterwards, with the prosecution of the discharge, a gradual and slow recovery, was observed and the reduction in area reach again the initial levels. These results lead to suppose that the kind of process, initiated within the material, in the region where the hydrogen concentration passes a given level, is the formation of molecular hydrogen, especially in contact with some types of inclusions acting as catalysts. This should favour the formation of channels, in correspondence to the areas having the higher segregation or cavities, or intergranular cracks, according to the density of discharge [11].

Fig. 5 and 6, show the results of the thermal analysis on AISI 420 steel full annealed and hardened respectively specimens. Hydrogen extracted from full annealed steel was higher than that from hardened steel; this may be because diffusivity in the annealed is higher than the martensitic microstructure (Tab. 3, [12]), even if martensitic structure has higher solubility (about twice) than ferrite, as referred by Johnson [13], Thompson and Robertson [14].

**TABLE 3 - (12) Atomic hydrogen solubility values for AISI 420 stainless steel at 300 K (27 °C)**

|                   | Solubility<br>(ml H <sub>2</sub> /100 g) | Solubility<br>(p p m) | Permeability<br>(mol m <sup>-1</sup> s <sup>-1</sup> ) | Diffusivity<br>(m <sup>2</sup> s <sup>-1</sup> ) |
|-------------------|--|-----------------------|--|--|
| AISI 420 Annealed | 9.1                                      | 8.1                   | 1.41 exp-9   | 2.25 exp-11                                      |
| AISI 420 Quenched | 78                                       | 70                    | 1.95 exp-9   | 3.60 exp-12                                      |

The results of tests of thermal analysis after 24 hours charging showed a significant decrease in degasing quantity of hydrogen under temperature of 400 °C, while slighlthy change upper this temperature. These tendencies were higher for quenched specimens (Fig. 7 and 8).

Considering the diagrams of thermal analysis obtained with different charging times it is evident that with the improvement of time from 30' to 3000' te peak amplitude of hydrogen degasing under 400 °C is the main aspect that characterize the particular level of hydrogenation of steel. No difference at all is possible to see over 600 °C in annealed structure analysis among the tests characterized by different time of charging (Fig. 9 and 10), while in quenched structure analysis an increasing trend upper 600 °C is observed (Fig. 11 and 12).

These tendencies were the same for two kinds of structure examined and the motive of this trend may be because the strong trap sites are the first traps occupied, and with the improvement of charging time, the quantity of degased hydrogen from weak trap sites increases.

From the slope of diagrams of Fig. 5 and 6 is possible to see for the charging of 1000' there is the maximum level of hydrogen fraction with low binding energy. This observation has a correlation with the fall of toughness of AISI 420, according one of the authors [9], afterwards, with the prosecution of the discharge there is a gradual recovery.

A metallurgical interpretation of the different trap sites that were obtained from results of thermal

analysis could be done considering the interaction energy. Very weak trap sites as dislocations fine precipitates in matrix seem to be almost totally degased within 24 hours at room temperature (range A). The difference between analysed quantity immediately after charging and that at 24 hours after charging is a quantity consisted with hydrogen from weak trap sites and diffusible hydrogen. Intermediate trap sites, particularly in quenched specimens, were put in evidence with degasing in the range 400-600 °C. Strong trap sites, which remained even 24 hours after charging were degased at temperature between 600 °C and 800 °C (range C). This kind of trap sites appeared only in specimens with hardened structure of AISI 420.

## Conclusions

The obtained results give us motive to affirm that:

Hydrogen degased quantity, considering the sum of the different fractions of singular temperature ranges is no linear and no monotone function of charging time.

There is a difference of behaviour between annealed and hardened structure in AISI 420 stainless steel.

The quantity of degased hydrogen from ferritic structure is higher than martensitic one. The reason of this phenomenon is the higher diffusivity of hidrogen in the annealed structure, even if the quenched structure has higher solubility and permeability of hydrogen.

The analysis carried out 20 min. after the end of charging has a high quantity of degased hydrogen under 400 °C; during the thermal analysis carried out 24 h after the end of charging, the hydrogen from weak trap sites, as dislocations fine precipitates in matrix is almost totally escaped.

The plot of total degased hydrogen versus time of charging are no monotone and has a maximum for 1000' of charging, for quenched and annealed steel. This trend has a correlation with the fall of toughness of annealed AISI 420 and it's gradual recovery [9], that is considered an effect of hydrogen with lower binding energy as diffusible hydrogen.

## References

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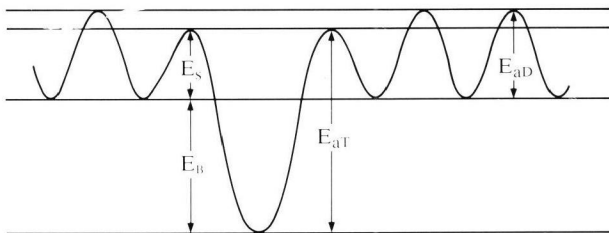


Fig. 1:  
The energy level of hydrogen around the trap site.

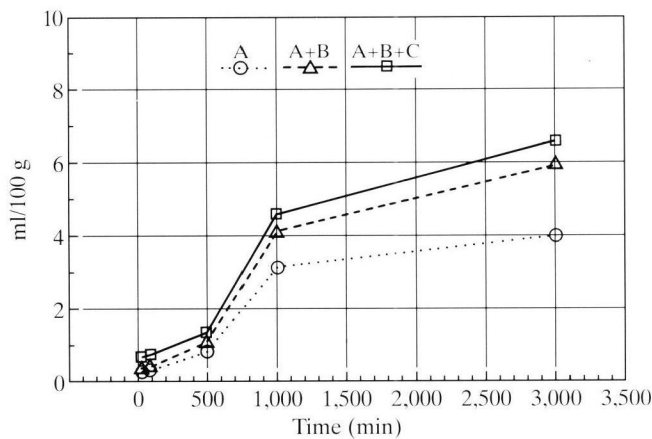


Fig. 3:  
Thermal analysis on Fe ARMCO.

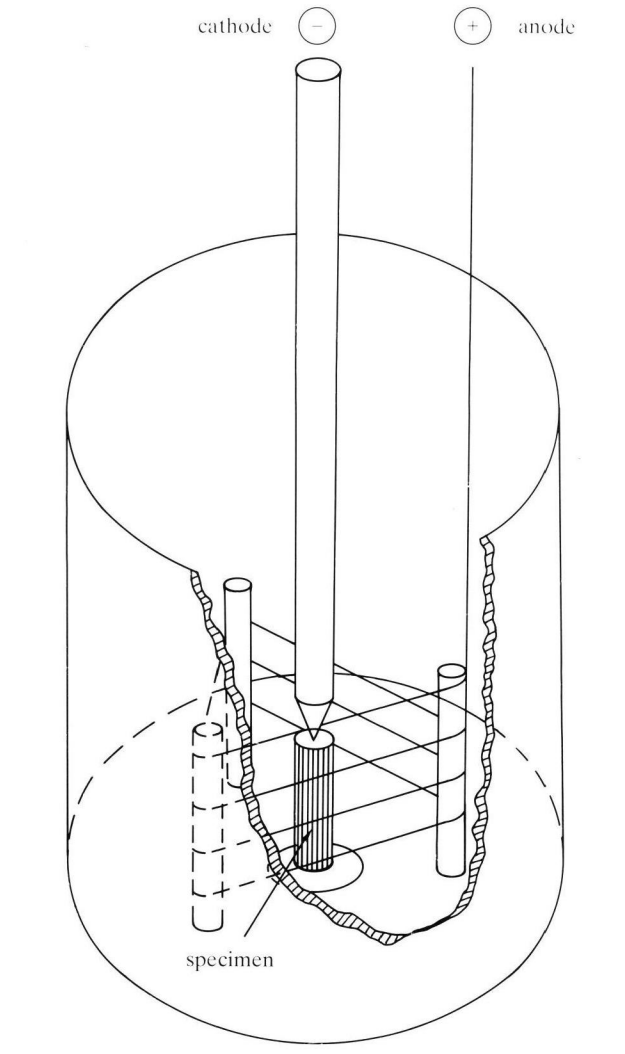


Fig. 2:  
Apparatus for cathodic charging of specimen.

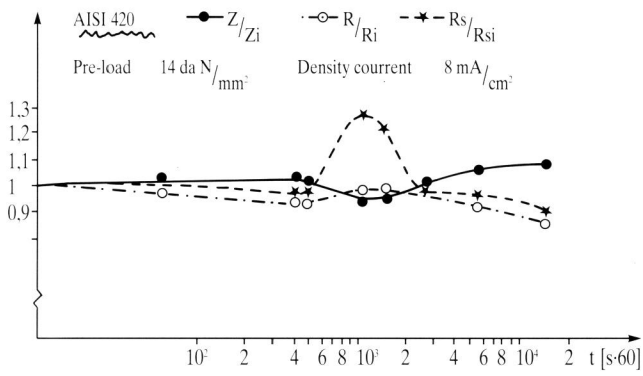


Fig. 4:

(11) Pre-aged fracture method. Function charging time - per cent of reduction in area reach again the initial levels.

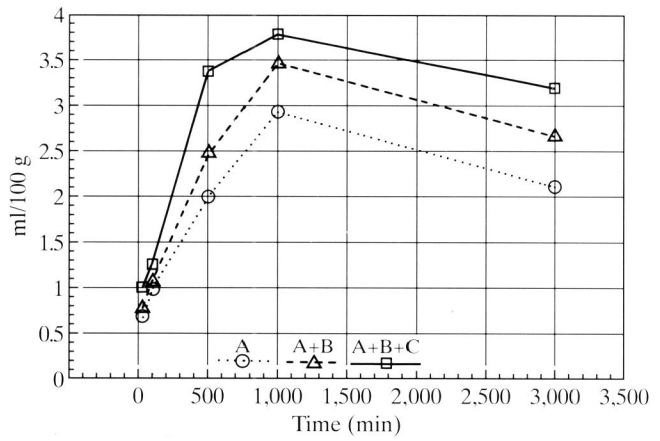


Fig. 5:

Thermal analysis on AISI 420 steel full annealed, carried out 20 min. after the end of cathodic charging.

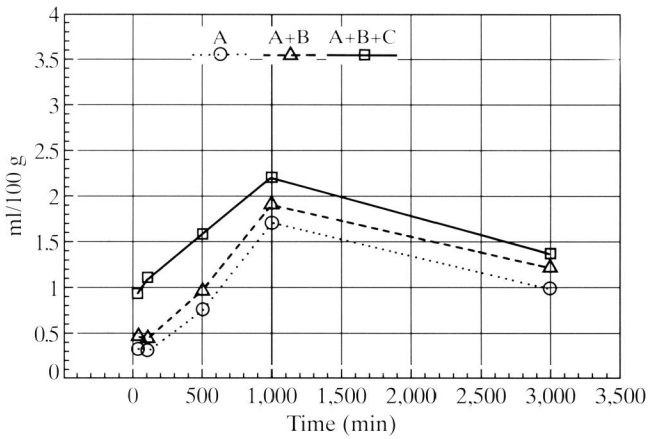


Fig. 6:

Thermal analysis on AISI 420 steel quenched, carried out 20 min. after the end of cathodic charging.

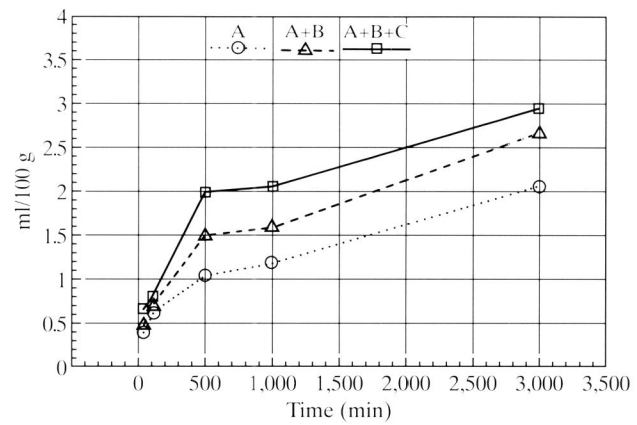


Fig. 7:

Thermal analysis on AISI 420 steel full annealed, carried out 24 hours after the end of cathodic charging.

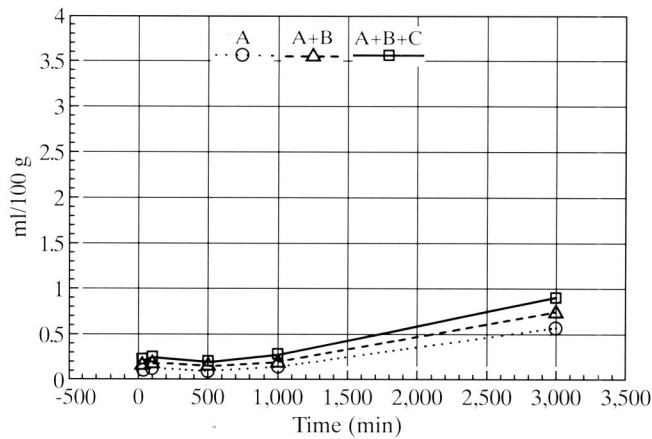


Fig. 8:

Thermal analysis on AISI 420 steel quenched, carried out 24 hours after the end of cathodic charging.

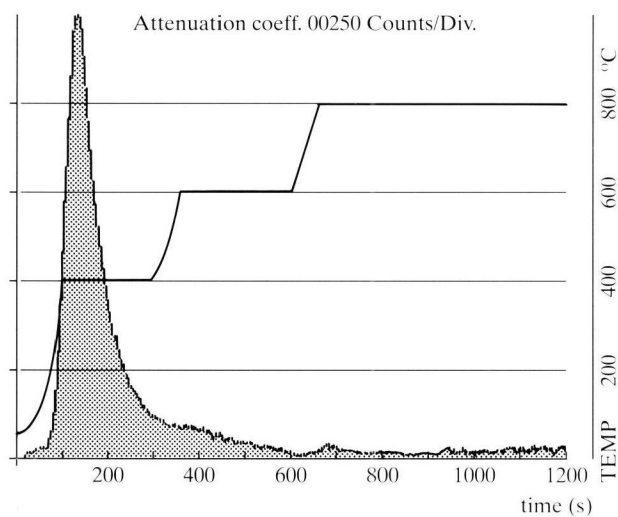


Fig. 9:  
Diagrams of degased hydrogen from AISI 420 steel full annealed, after cathodic charging of 1000 min. and analysed after 20 min. of break.

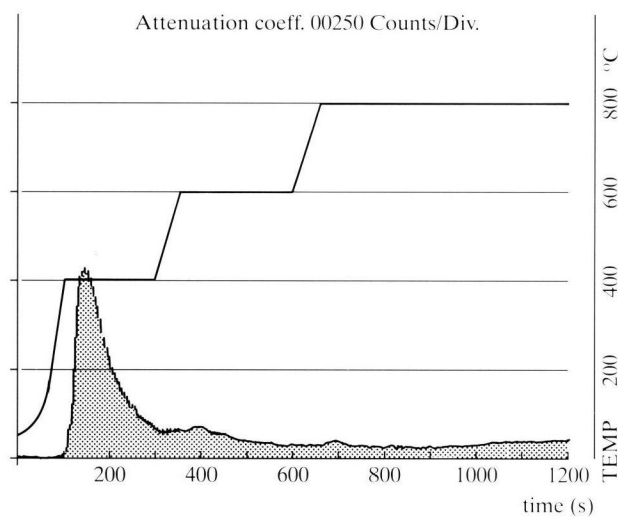


Fig. 10:  
Diagrams of degased hydrogen from AISI 420 steel full annealed, after cathodic charging of 1000 min. and analysed after 24 hours of break.

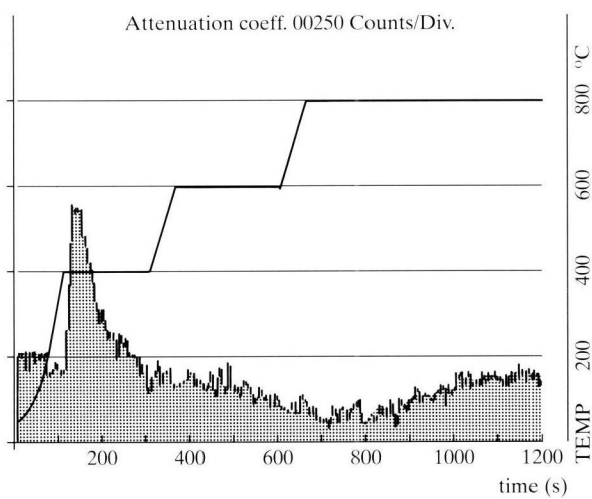


Fig. 11:  
Diagrams of degased hydrogen from AISI 420 steel hardened, after cathodic charging of 1000 min. and analysed after 20 min. of break.

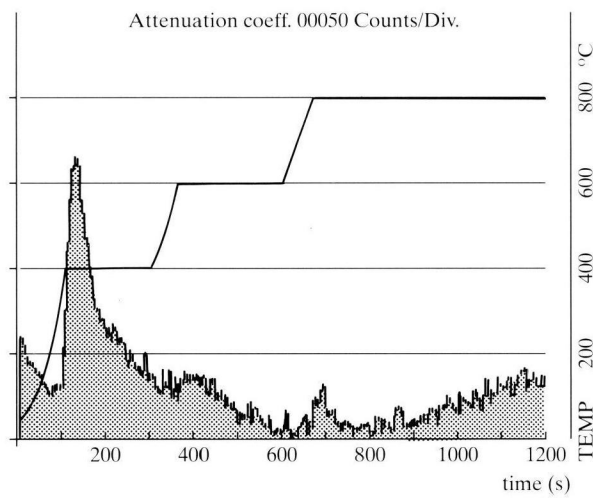


Fig. 12:  
Diagrams of degased hydrogen from AISI 420 steel hardened, after cathodic charging of 1000 min. and analysed after 24 hours of break.