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NASA
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NASA TM-103537

THE EFFECT OF STRESS ON HYDROGEN UPTAKE AND DESORPTION BY A-286

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May 1991

(NASA-TM-103537) THE EFFECT OF STRESS ON HYDROGEN UPTAKE AND DESORPTION BY A-286 (NASA) 19 p
CSCL 11F
N91-28341
Unclas
G3/26 0019916

National Aeronautics and
Space Administration
George C. Marshall Space Flight Center

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF TABLES

TECHNICAL MEMORANDUM

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INTRODUCTION

The present work was undertaken to provide further information regarding the effect of tensile stress on the hydrogen distribution in metals on charging and also on the effect on other parameters which might be involved, such as the hydrogen diffusion coefficient. In this case, only the effect of tensile stress was studied. The material chosen for investigation was the A-286 alloy because it is highly resistant to hydrogen embrittlement and can withstand rather high stresses when charged with hydrogen. The investigation was carried out only in the elastic region since determination of the hydrogen diffusion coefficient is a sensitive function of the sample radius, and deformation of the sample in the plastic region would prevent accurate determination of this parameter.

Several other studies concerning the influence of stress have been carried out. Wriedt and Oriani [1] showed that an elastically stressed 75-percent Pd to 25-percent Ag alloy in a hydrogen atmosphere increased in hydrogen content under uniaxial tension and decreased in hydrogen content under uniaxial compression. Bockris, et al. [2] studied Armco iron and 4340 steel and found that permeation of hydrogen was increased by tensile stress and decreased by compressive stress with the diffusion coefficient being unaffected by the applied stress. Waisman, Sines, and Robinson [3] measured the equilibrium pressure of hydrogen at elevated temperatures in C.P. titanium and Ti-6Al-4V alloy as a function of applied stress and found the expected decrease in activity with tensile stress and an increase in activity with compressive stress. Also, Schaumann, Volki, and Alefeld [4] used Gorsky effect measurements, i.e., relaxation strain accompanying point defect migration under a stress gradient, to determine the diffusion coefficient of hydrogen in V, Nb, and Ta.

This paper presents results from A-286 specimens under stresses of 0, 233 MPa (33.9 ksi), 467 MPa (67.7 ksi), 700 MPa (101.55 ksi), and 840 MPa (121.86 ksi). These stresses represent 0, 25, 50, 75, and 90 percent of the yield point, 933 MPa (135.4 ksi). Calculations were made using the standard method previously described [5] for data at large time (0 to 150,000 s) and with a new method involving only the data at small times (0 to 10,000 s), and which employs the method of least squares and makes use of a nonlinear least-squares program developed by Busing and Levy [6].

CALCULATION OF HYDROGEN DESORPTION CURRENT AT SMALL TIME

In the case of absorption by a circular cylinder of radius $r = a$ where a constant surface concentration C_o is maintained, and the medium is initially free of solute, the solution to the diffusion equation for radial flow may be given in terms of Bessel's function of the first kind and of zero order, $J_o(X)$, and its differential $J_o'(X)$. The hydrogen concentration in the cylinder as a function of r for a medium from which hydrogen is being desorbed is

$$C(r) = \frac{2}{a^2} \sum_{1}^{\infty} e^{-D\alpha_n^2 t} \frac{\int_0^a rf(r)\, J_o(\alpha_n r)\, dr}{[J_o'(\alpha_n a)]^2} J_o(\alpha_n r) \tag{1}$$

where α_n is the nth root of the equation $J_o(\alpha_n a) = 0$. The first two roots of $J_o(\alpha_n a) = 0$ are

$$\alpha_1 = \frac{2.405}{a} \qquad \text{and} \qquad \alpha_2 = \frac{5.520}{a} \tag{2}$$

where a is the sample radius. In the present case, a total of eight such roots were used. The functions $J_o(X)$ and $J_o'(X)$ are given by the series

$$J_o(X) = 1 - (\tfrac{1}{2}X)^2 + \frac{(\tfrac{1}{2}X)^4}{1^2 \cdot 2^2} - \frac{(\tfrac{1}{2}X)^6}{1^2 \cdot 2^2 \cdot 3^2} + \ldots \tag{3}$$

$$J_o'(X) = -(\tfrac{1}{2}X) + \frac{(\tfrac{1}{2}X)^3}{1^2 \cdot 2} - \frac{(\tfrac{1}{2}X)^5}{1^2 \cdot 2^2 \cdot 3} + \ldots \tag{4}$$

and their values for any value of X are given in the tables. The mean or observed hydrogen concentration in the cylinder is given by

$$\bar{C} = \frac{2}{a^2} \int_0^a f(r) r\, dr \tag{5}$$

In the above equations, $f(r)$ is given by

$$f(r) = C_o \left(1 + \frac{2}{a} \sum_{1}^{\infty} \frac{1}{\alpha_n} \frac{J_o(\alpha_n r)}{J_o'(\alpha_n a)} e^{-D\alpha_n^2 t} \right) . \tag{6}$$

The function $f(r)$ represents the hydrogen concentration profile obtained on charging the sample with hydrogen. Here C_o is the apparent surface concentration of hydrogen, and t is the time of charge. The amount of hydrogen $Q(t)$ which has diffused out of the cylindrical medium per unit length after time t is:

$$Q(t) = Q_{HM}^{\infty} - 2\pi \int_0^a C(r)\, r\, dr \quad . \tag{7}$$

The current at time t in μA/cm is given by:

$$I(t) = 0.6015146\, d \int_0^a \frac{d}{dt}\,[rC(r)dr] \times 10^6 \quad . \tag{8}$$

The factor 0.6015146 is necessary to convert ppm-cm^2 to coulombs/cm, and d is the metal density.

The above equations were incorporated into a general nonlinear least-squares program ORGLS [6] with the variables D and C_o being determined by iteration to convergence. The mean hydrogen concentration in the cylinder was subsequently determined using these parameters and equation (5). The general treatment for reduction of data at large time has been given previously [5].

EXPERIMENTAL

The EG&G-PARC model 350A corrosion measurement console was employed for the electrochemical measurements of hydrogen desorption. Samples consisted of tensile specimens of A-286 which were 5.08-cm (2-in) long with a gauge length of 1.905 cm (0.75 in) and a diameter of 0.3175 cm (0.125 in). The specimens were threaded at both ends with 1/4-20 NC threads. All metal parts except for the gauge section were coated with Miccromask stop-off lacquer to prevent electrical contact. The specimens were mounted on a Korros data slow strain rate (SSR) machine, enclosed in a glass cell having a 1 liter capacity. The cell was filled with a 0.1 N sodium hydroxide (NaOH) solution which provided the medium for charging of the sample with hydrogen and for conduction of the hydrogen desorption current. The SSR machine was then driven to the proper load level, which was maintained throughout the charging and desorption stages. Sample blanks were run at a constant potential of +0.25 V (NHE). The period of measurement was 150,000 s for each sample with values of the current being recorded every 500 s. The specimens were then charged with hydrogen for a period of 1 h at a current density of 90 mA/cm^2. Measurements of the desorption current were initiated immediately on completion of charging with current measurements being taken exactly as for the blanks. After completion of each run, data were read to an IBM PC/AT computer for calculation purposes. Currents due only to hydrogen were obtained by subtraction of the currents for blanks. After data from both the hydrogen containing sample and its corresponding blank were obtained, the experimental curve, $Q(t)$ versus time, was obtained through integration of the current-time curves. Values of Q^{∞}_{HM}, the observed concentration $\bar{C}$, the apparent surface concentration C_o, and the hydrogen diffusion coefficient D were obtained according to the methods described previously [5]. Theoretical curves were calculated using the program PDEONE [7]. In addition, values of C_o, $\bar{C}$, and D were obtained using the desorption current at small time (0 to 10,000 s) according to the method described in this report.

Residual hydrogen concentrations were determined using a Leco Model RH2 hydrogen analyzer. The gauge section of the tensile specimen was retained after removing the remaining metal sections at each end with a diamond saw. Calibration of the hydrogen analyzer was accomplished with samples of known hydrogen concentrations.

RESULTS AND DISCUSSION

The A-286 CRES test material is identified in table 1. Observed and theoretical curves for hydrogen desorption are shown in figures 1 through 5 for stress levels of 0, 25, 50, 75, and 90 percent of yield. According to results obtained from the complete data sets, the percent hydrogen distribution uniformities in the samples are 23, 48, 88, 62, and 64 for the 0-, 25-, 50-, 75-, and 90-percent yields, respectively. Thus, the percent uniformity approaches a maximum at the 50-percent yield level and drops to lower values at higher stress levels. The least-squares fit of a third-degree polynomial to the uniformity versus percent yield is shown in figure 6. Results are summarized in table 2 for parameters calculated from data at large times and in table 3 for data at small times. The parameter values listed in table 2 are considered more reliable since they are derived using the entire data set (0 to 150,000 s) while those in table 3 are derived in the time range 0 to 10,000 s only. According to table 2, the value of the hydrogen diffusion coefficient D does not change appreciably over the entire stress range, in agreement with the results of Bockris, et al. [2]. The value of C_o, the apparent surface concentration of the hydrogen, increases to a maximum at the 50-percent stress level, dropping off thereafter. The mean hydrogen concentration C follows the same trend.

It is likely that the hydrogen distribution uniformity is governed by the permeability of the sample to hydrogen penetration. For a thin membrane, the permeability is given by

$$\text{Permeation} = \frac{DSP}{L} \tag{9}$$

Here, D is the hydrogen diffusion coefficient, S is the solubility of hydrogen, P is the exterior hydrogen pressure, and L is the membrane thickness. Thus, the percent uniformities follow the same trends as C_o and $\bar{C}$. The value of D is probably no different for hydrogen absorption from that measured in the desorption process. The hydrogen distribution uniformities depend on factors related to the solubility of hydrogen in the metal.

Trapped or residual hydrogen contents at each stress level are shown in table 4 along with the mobile hydrogen and total hydrogen concentrations. The percent trapped hydrogen is largest at 0 stress and smallest at 90-percent yield, and seems to follow this trend all the way although there is considerable scatter in the results, especially at 75-percent yield. Such a trend would be in agreement with a result obtained earlier [8] for ELI Ti-5Al-2.5 Sn, where it was found that the metal lost approximately half of its trapped hydrogen during a 1 month period when placed under a high tensile stress (75 percent of yield).

CONCLUSIONS

The major effect of tensile stress is to increase the permeation of hydrogen into the metal and to increase uniformity of the hydrogen distribution in the metal. In this study, the apparent surface hydrogen concentration C_o, the mean hydrogen concentration $\bar{C}$, and the hydrogen distribution uniformity all increased up to a stress level 50 percent of yield and decreased thereafter. The diffusion coefficient D was relatively unaffected by stress. The percent of trapped hydrogen generally seems to decrease with increasing stress which would be in agreement with a result obtained previously in this laboratory [8], although there may be some doubt as to the consistency of the trend. Metals other than A-286 will be studied at a future time, but it is believed that the results obtained in this investigation are indicative of the general effect of stress on hydrogen-metal behavior.

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Table 1. Chemical analysis of A-286 CRES.

Elements	Specifications (MIL-STD-163)	MSFC Analysis
Cu	-	0.08
V	0.10 - 0.50	0.28
Si	1.0 Maximum	0.25
B	0.003 - 0.10	0.007
Al	0.35 Maximum	0.27
Ti	1.90 - 2.35	2.24
Mo	1.00 - 1.50	1.09
Mn	2.0 Maximum	0.19
Fe	Balance	57.33
Ni	24.0 - 27.0	24.43
Cr	13.5 - 16.0	13.77
P	0.025 Maximum	0.014
C	0.08 Maximum	0.05
S	0.025 Maximum	0.001

Table 2. Parameters calculated from data at large time.

% Yield	$Dx10^8$ cm²/sec	C_o* ppm	$\bar{C}$** ppm	% Uniformity
0	4.17	31.11	5.49	23
25	2.17	68.96	8.62	48
50	2.04	73.95	8.97	88
75	2.35	51.92	6.73	62
90	2.47	64.58	8.57	64

*Apparent hydrogen concentration at sample surface.
**Mean hydrogen concentration in sample.

Table 3. Parameters calculated from data at small time (0–10,000 s).

% Yield	$Dx10^8$ cm²/sec	C_o* ppm	$\bar{C}$** ppm
0	6.88	33.70	7.18
25	5.36	48.75	9.22
50	3.15	41.70	6.12
75	3.55	40.24	6.25
90	4.44	44.82	7.74

* Apparent hydrogen concentration at sample surface.

** Mean hydrogen concentration in sample.

Table 4. Hydrogen trapping as a function of stress.

% Yield	Mobile Hydrogen ppm	Trapped Hydrogen ppm	Total Hydrogen ppm	% Trapped Hydrogen
0	5.49	0.68	6.17	10.9
25	8.62	0.96	9.58	10.0
50	8.97	0.40	9.37	4.3
75	6.73	0.77	7.50	10.3
90	8.57	0.20	8.77	2.3

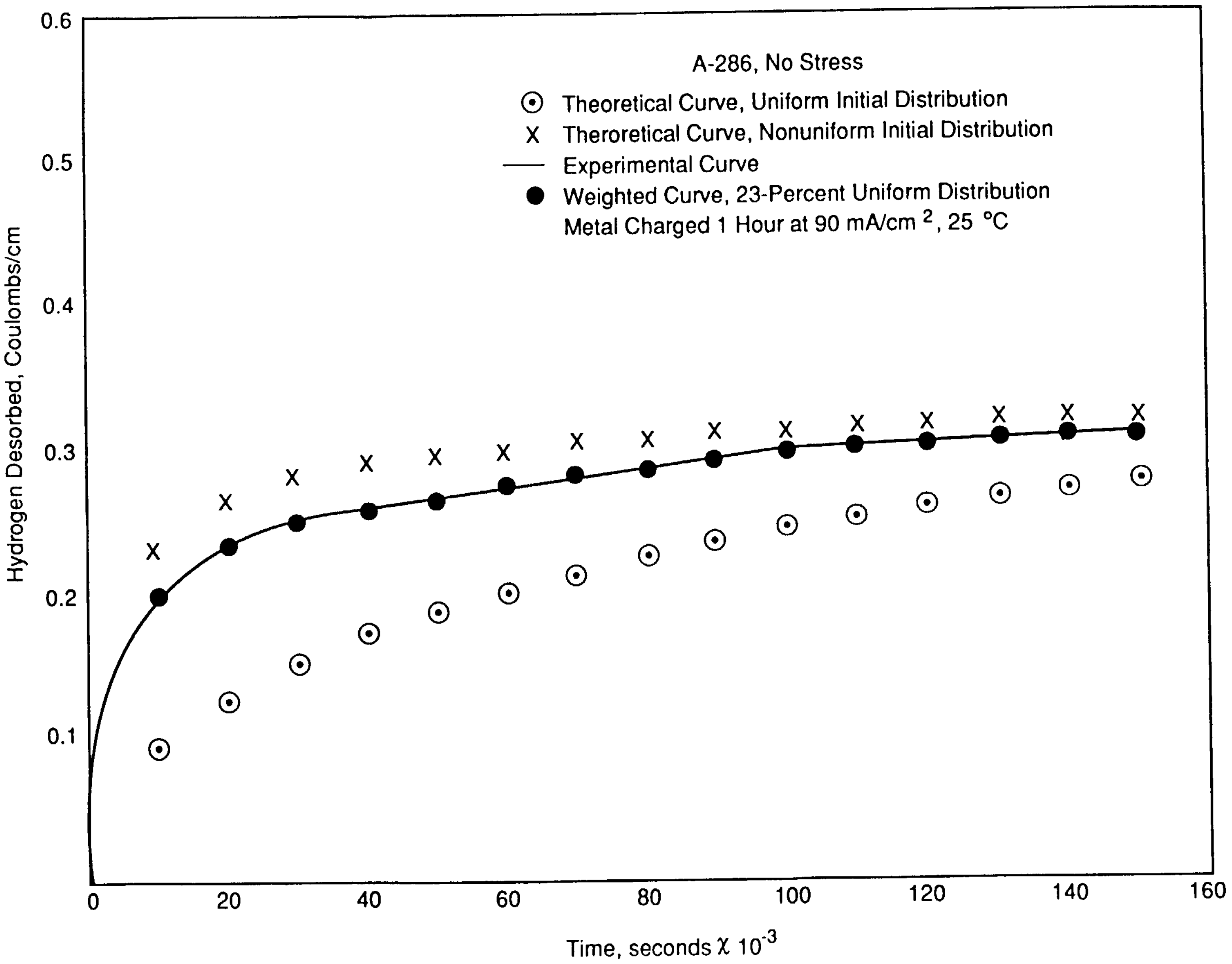

Figure 1. Hydrogen desorption curves for A-286 at zero stress.

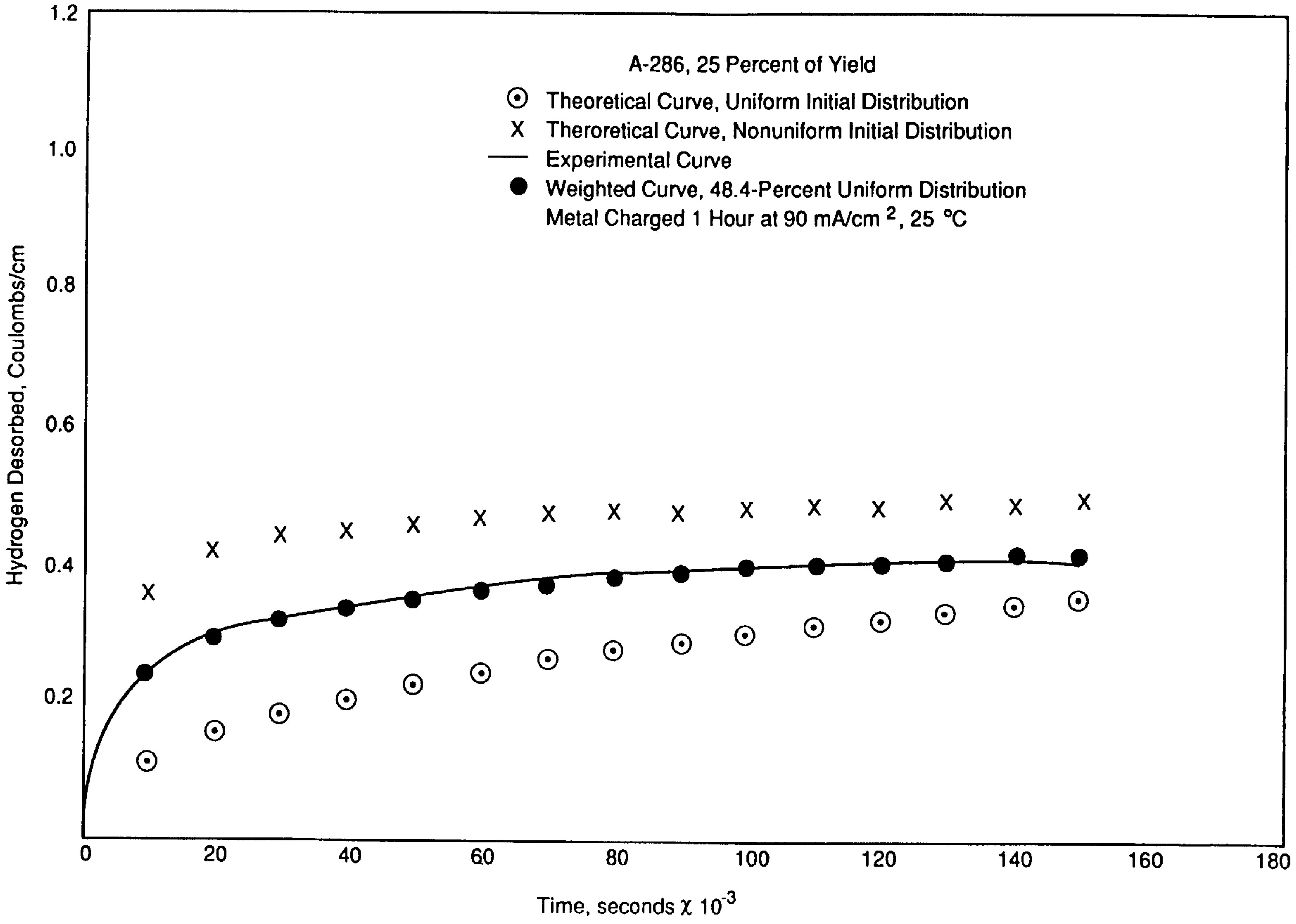

Figure 2. Hydrogen desorption curves for A-286 at 25-percent yield.

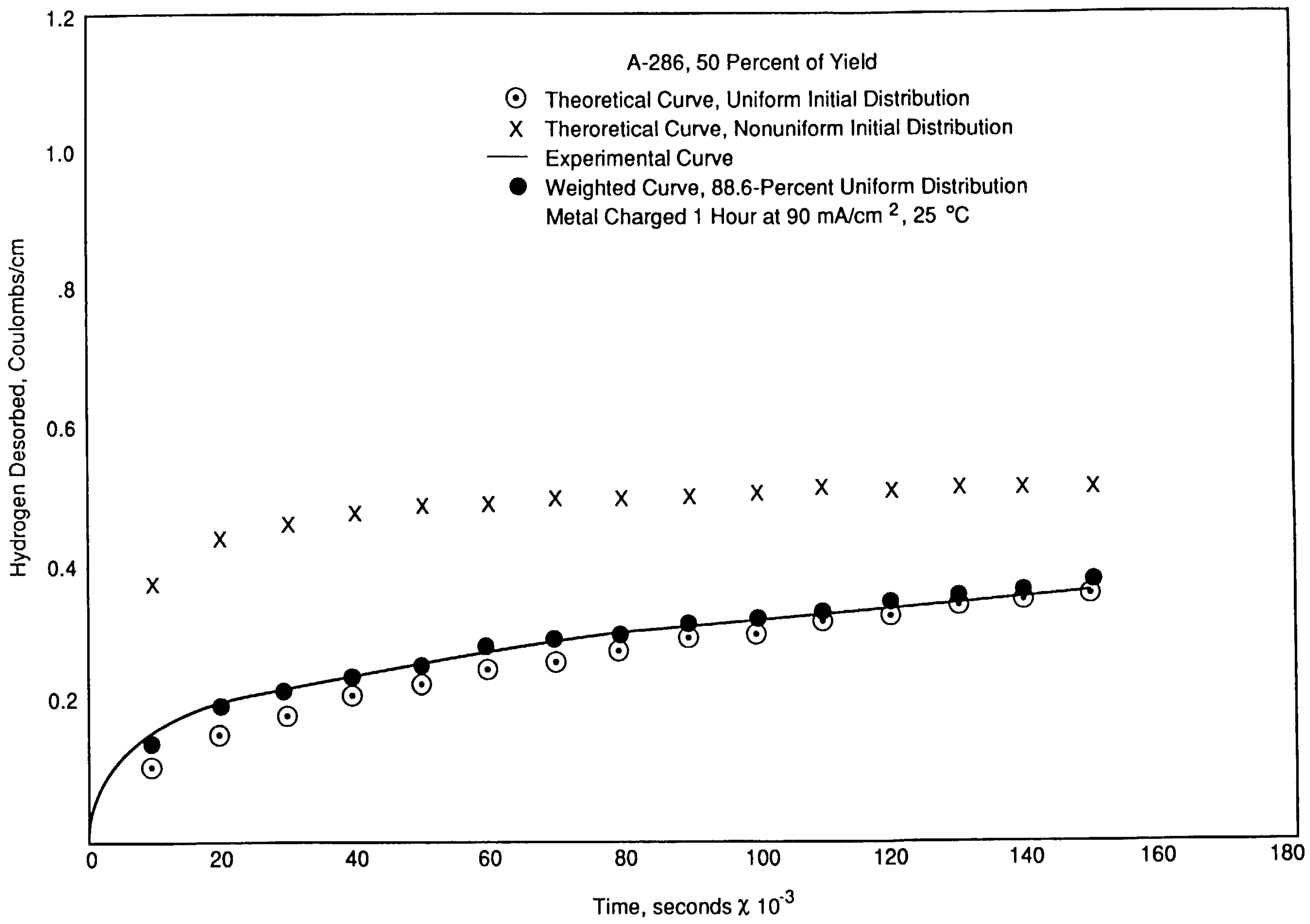

Figure 3. Hydrogen desorption curves for A-286 at 50-percent yield.

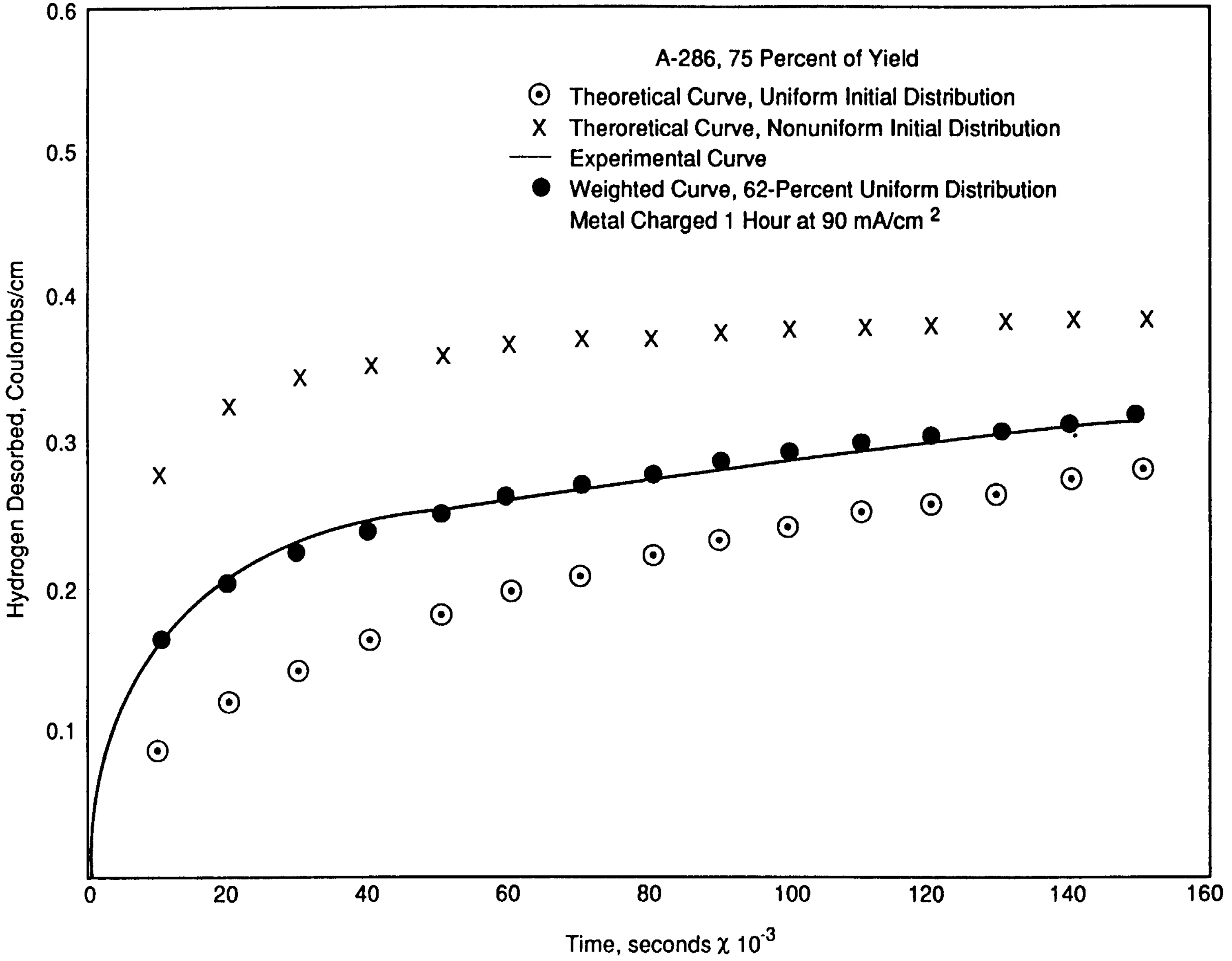

Figure 4. Hydrogen desorption curves for A-286 at 75-percent yield.

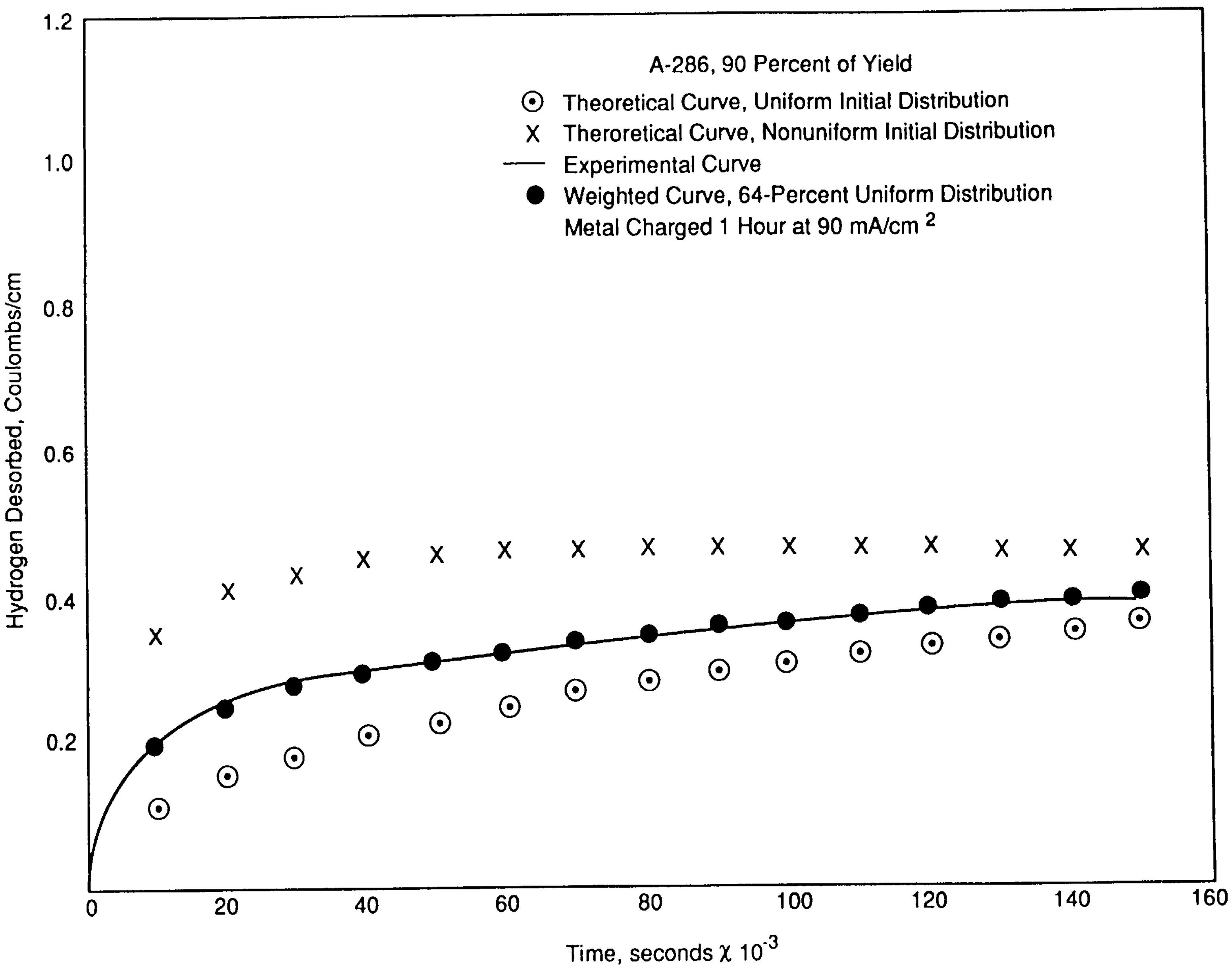

Figure 5. Hydrogen desorption curves for A-286 at 90-percent yield.