ELSEVIER

Journal of Alloys and Compounds 356–357 (2003) 240–243

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Peculiarity of hydrogen distribution in steel by cathodic charging

S.M. Beloglazov*

Department of Physical Chemistry, University of Kaliningrad, Alexander Nevski 14, 236041 Kaliningrad, Russia

Received 15 July 2002; received in revised form 6 December 2002; accepted 1 February 2003

Abstract

Steel surfaces of machines undergo corrosion protection most commonly by means of electrodeposited Zn, Cd, Ni, Cr etc. with chemical or electrochemical surface pretreatment for deposition. To preserve the surface geometry steel wire and strips undergo cathodic electrocleaning in an alkaline bath and cathodic etching or pickling in acid solutions. A major obstacle to progression in our knowledge of hydrogen absorption (HA) by metals in the above processes was a lack of techniques for determining the hydrogen distribution in steel, resulting from electrochemical processes at the steel surface. Determination of hydrogen absorbed in the processes of corrosion, cathodic etching and electroplating of metal coating was carried out by means of anodic dissolution of steel. This technique was specially adapted to determine the distribution of electrochemically absorbed hydrogen in steel. For gathering information on the behaviour of hydrogen inside the metal and the deterioration of its stress-related properties, the method of anodic dissolution of steel has no equal. By applying the anodic dissolution technique we were the first to establish the concentration profile of hydrogen in metals (steels, titanium alloys). All the hydrogen absorbed by the cathodically treated metal was found to be distributed in a thin surface layer ($\delta < 0.1$ mm for carbon steels), and this layer is responsible for changes in the plasticity and fatigue of steel under static or dynamic loading. The same characteristic is found in the hydrogen distribution in substrate metal (steel) as a result of electrodeposition processes. Peculiarities of the absorbed hydrogen distribution in steel under cathodic polarisation is the aim of the present paper. Examples of experimental data for steel corrosion, Zn and Cd electrodeposition are presented.

Keywords: Electrode materials; Surfaces and interfaces; Electrochemical reactions

1. Introduction

Hydrogen belongs to the most familiar contaminants of metal. Hydrogen absorption (HA) by steels, particularly high-strength steels and titanium alloys, results in considerable loss of their mechanical properties: plasticity, and their ability to withstand static sustained loads and dynamic cyclic loading. Delayed hydrogen fracture and fatigue damage of steel very often arise from hydrogen absorbed by steel in metallurgical processes, where hydrogen turns out to be almost uniformly distributed within steel parts, and because of this, vacuum melting or ‘hot extraction’ techniques are appropriate for the case.

The use of steel as a main material in the metal working industry, oil and gas production and transport, shipbuilding, wagon building etc. results in huge losses from corrosion. Air and water pollution by industrial pollutants accelerate metal corrosion and increase hydrogen absorption by corroded steel (processes with hydrogen depolarizing cathode). It is known that hydrogen sulphide, inorganic compounds of As, Sb and Se accelerate hydrogen absorption by factors of 10–100 [1]. Steel wire and strips undergo cathodic electrocleaning in alkaline baths and cathodic etching or pickling in acid solutions. The current efficiency of metal electrodeposition can never be 100%: actually, during industrial electroplating processes from 2 to 87% of current is lost for Me deposition on the cathode and wasted on hydrogen evolution. A portion of hydrogen adatoms is absorbed by the subsurface layer of steel. A major obstacle to progress in our knowledge of HA by metal in the above processes was a lack of techniques for determining the absorbed hydrogen distribution character in steel because vacuum melting or ‘hot extraction’ techniques are not appropriate for the acquisition of data, characterising hydrogen in steel, resulting from electrochemical processes at the steel surface. More advanced techniques have been developed for analysing the absorbed hydrogen distribution within a metal, which is essential to our understanding of material failure due to hydrogen

---

*Corresponding author.

E-mail address: smbeloglazov@mail.ru (S.M. Beloglazov).

0925-8388/03/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/S0925-8388(03)00354-2

embrittlement of steel and Ti alloys, resulting in corrosion processes with H-depolarising cathode, acid pickling and metal electroplating.

Bardenheuer and Ploum [2] disclosed that hydrogen content (HC) measured in p.p.m. using the 'hot extraction' technique was the reciprocal of the diameter of iron wire subjected to cathodic hydrogen charging. Smialowski et al. [3,4] obtained the same results on Fe, Ni an Co. Several results of other authors [5,6] suggest an unequal distribution of hydrogen absorbed by steel cathodes and confirm the specific role of surface layers of metal in H diffusion and HA. We used anodic dissolution of the steel specimen and registration of the hydrogen released from collectors (traps—in case of atomic dimensions and microscopic crystal defects) and the metallic solid solution, to estimate the function of distribution of H inside the steel cathode [7,8].

2. Peculiarity of cathodic hydrogen distribution in metal

The main sources of hydrogen supply in metals are metallurgical, welding and electrochemical processes at the interface: metal–water solution of electrolyte, even though such cases, as use of hydrogen as secondary energy carrier (water splitting, hydrogen pipelines and storage tanks), may be disregarded. Adsorbed H atoms can appear on the metal surface and this leads to diffusion of H inside the metal. The diffusion coefficient D_H obtained by the delay time estimation was found to be strongly dependent on layer thickness. D_H varies from 0.7×10^{-8} to 2×10^{-5} $cm^2\cdot s^{-1}$ with thickness $\delta=0.1$–0.9 mm [9,10]. The final value $D=2\times10^{-5}$ $cm^2\cdot s^{-1}$ remains the same for thicker layers. The HC (V_H, ml/100 g of metal sample on the whole, or p.p.m.) absorbed by iron wires of different diameters d during cathode polarisation for a long period in an H_2SO_4 solution with added As_2O_3 (as HA promoter) decreased with increased d [11]. Raczynski and Smialowski confirmed these results [12]. The hydrogen penetration depth of 0.64 mm in 1 h of cathodic polarisation of SAE 1020 steel in 4% H_2SO_4 was found [6] by measuring the change of plasticity of steel specimens immediately after cathodic polarisation and after successive stripping of subsurface layers of steel by cutting or anodic dissolution. Similar results were noted earlier [5]. Thus, several experimental results suggest an unequal distribution of HC into steel cathodes and confirm the specific role of the surface layers of a metal in H diffusion and absorption.

There was an indirect confirmation of hydrogen-rich layer formation in mild steel with 0.08% C. The microhardness of a 50 μm subsurface layer of steel 10 increases from 2150 $MN\cdot m^{-2}$ in initial state to 3430 $MN\cdot m^{-2}$ after cathodic polarisation for 1 h by 100 $A\cdot m^{-2}$ in a 0.1 N H_2SO_4 solution with 2.5 $mg\cdot l^{-1}$ H_2SeO_3 added as promoter of hydrogen absorption. It increases to 4500 $MN\cdot m^{-2}$ when current density (c.d.) 500 $A\cdot m^{-2}$ is used [7]. Microhardness decreases gradually as the depth in steel increases and beginning from 0.4 mm, microhardness was at its initial level. Ten hours of hydrogen charging produced an increase in steel microhardness from 2.86 to 9.0 $GN\cdot m^{-2}$ in a subsurface layer of only 30 μm [1].

3. Experimental techniques for cathodic hydrogen distribution study

Anodic dissolution of steel and measuring the hydrogen released from internal collectors and metallic solid solutions was used for the first time to estimate the function of distribution of hydrogen inside the steel cathode in an H_2SO_4 solution [7,13,14]. Later this technique was used for HC analysis of electroplated steel [15–20] as well as for analysis of corroded steel [21–27]. We used a porous ceramic cylinder for the anolyte and an external glass container for the catholyte with a copper cathode. Measurement of the gaseous hydrogen liberated from the steel being dissolved was made by means of a gas-burette over the steel specimen [1,7]. Anodic c.d. must not exceed that needed for a potential rise to O_2 evolution, in order to avoid the distortion of results. It may be 150–250 $A\cdot m^{-2}$ for mild and carbon steel. The mass loss of a specimen allows the HC to be found at any dissolved steel layer. By means of graphs representing HC as a function of depth from the outside steel surface it is possible to depict the average HC for 10–15 μm thickness of each metal layer. Bonding the middle points of each anodic dissolved layer, a smooth curve will be obtained. A porous cylindrical porcelain germ-proof filter with a glazed funnel-like upper part (the microburette is fastened to them) could serve as a diaphragm for the anolyte. The rubber stopper in the bottom has a screw for specimen fastening and connecting to the circuit. An important feature of this device is equal metal dissolution throughout the length of the specimen. An improved variant of this technique is based on evaluation of the decreased concentration of O_2 dissolved in the anolyte after interaction in the presence of a Pt-catalyst with hydrogen, resulting from the dissolved steel specimen. The concentration of O_2 before and after anodic dissolution of a thin (e.g. 10–15 μm of thickness) steel layer is determined spectrophotometrically by the use of safranine T as a leuco base [19–27].

A variant of this technique involves the use of the amperometric reduction method for O_2 concentration measurement. The biological Microanalyser OP-210/3 has a special two compartment device and the reduction current of dissolved O_2 passed through the polypropylene membrane to the Pt-cathode sustained by a constant potential allows oxygen content to be measured [16,21].

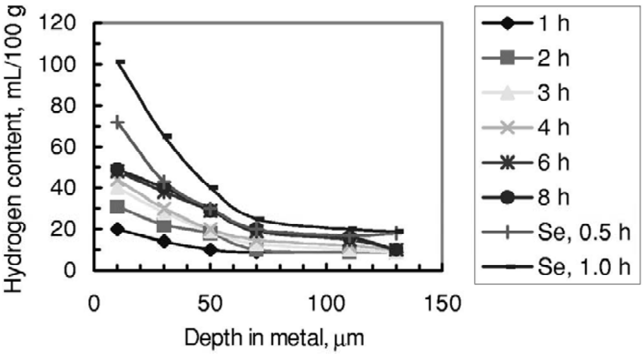

Fig. 1. Hydrogen concentration profiles in steel with 0.8% C after cathodic pickling (100 A·m^{-2}) in 0.1 N H_2SO_4 for 1–8 h and with addition of 2.5 mg·l^{-1} H_2SeO_3 at 0.5 and 1 h.

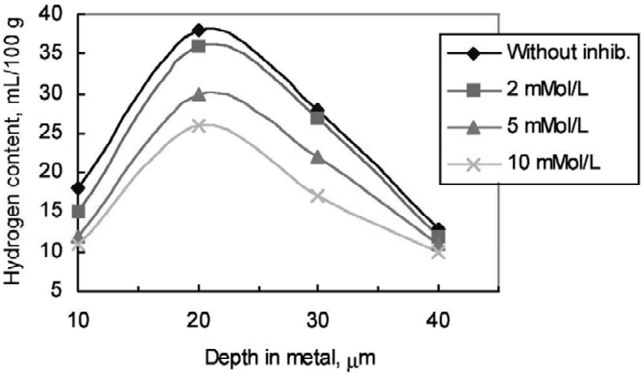

Fig. 3. Hydrogen concentration profiles in steel with 0.08% C after corrosion for 200 h in aqueous salt media with H_2S produced by sulphate-reducing bacteria and corrosion inhibitor.

4. Examples of cathodic hydrogen distribution in metals

Figs. 1 and 2 show the hydrogen distribution within a wire Ш 1.0 mm of carbon steel (ca. 0.8% C, 0.3% Mn, 0.2% Si) with a ferritic–pearlitic structure after cathodic pickling in 0.1 N H_2SO_4. As may be seen, HC increases when c.d. rises or pickling duration grows from 1 up to 6 h, but not to 8 h; H_2SeO_3 (promoter of HA) vastly increases the absorbed HC. Doubled pickling duration does not result in doubled HC (Fig. 1). It is reasonable to assume that in reality only the promoter of HA would be capable of driving absorbed hydrogen into the depth of the steel. Figs. 1 and 2 show a hydrogen-rich layer formation about 0.1 mm thick — in close agreement with ones obtained earlier [17,18].

A number of investigations have dealt with HA by steel corrosion, in particular in H_2S-containing media [17,18]. An example of hydrogen distribution in the depth of mild steel St.3 after corrosion in an aqueous salt medium (pH= 7.8) with sulphate-reducing bacteria is shown in Fig. 3.

The anode dissolution technique for HC determination in steel looks promising for electroplating. Fig. 4 shows the hydrogen distribution in Cd-plated (current densities 30–150 A·m^{-2}) carbon steel with 0.8% C. The cadmium was removed before anodic dissolution of the steel specimens. As seen, the biggest HC occurs in a subsurface steel layer ca. 20 μm thick. The first from Cd/steel interface layer has a lowered HC because it has opened outside H_2 collectors. The absorbed HC is a function of c.d. and bath composition; widely used organic brighteners may significantly reduce the HC of steel, but the inhibitors disclosed by us are especially effective [1,15–20].

These results and those of previous data may be explained by the existence of collectors in the metal, filled with molecular hydrogen absorbed by the steel subsurface layers in the corrosion or cathodic polarisation processes, which prevent deep penetration of hydrogen while diffusing in steel. The H-molisation process, while on the internal collector surface, results in a huge growth of partial H_2 pressure in the collectors. Further diffusion of H atoms into the metal depth has to take place through the already stressed and strained metal around the collectors. A plastic strain around H_2 collectors was detected earlier [28,29] as well as an increase of HC by stressed metal [30,31].

The hydrogen absorbed by the metal causes changes in

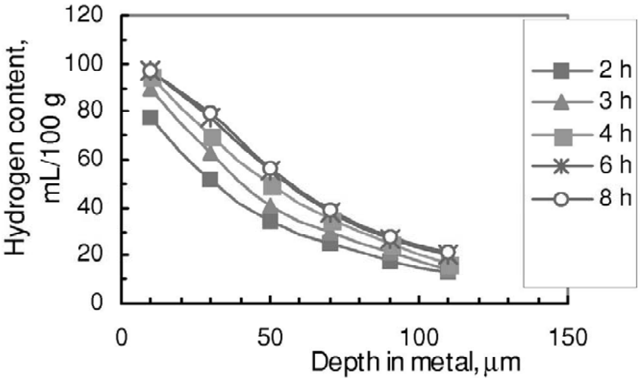

Fig. 2. Hydrogen concentration profiles in steel with 0.8% C after cathodic pickling (500 A·m^{-2}) in 0.1 N H_2SO_4 for 1–8 h.

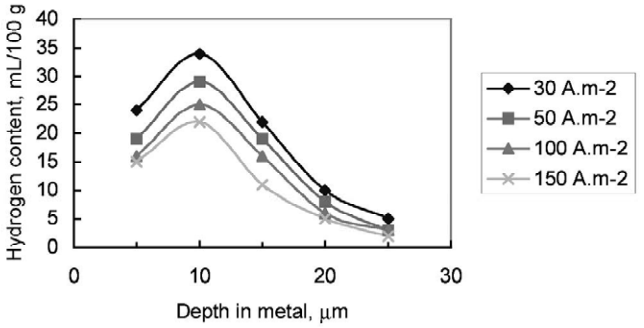

Fig. 4. Hydrogen concentration profiles in steel with 0.8% C after cadmium plating in a sulphate bath with current density 30–150 A·m^{-2}. Cd layer (δ=20 μm) was removed before steel anodic dissolution.

the energy state of the metal, promoting internal stresses and distortion of the crystal lattice [28]. This results in an increase in electrical resistance of such a Me–H system [30] and electrical conductivity correlation is possible between the dislocation quantity in the metal and the absorbed H atoms. It is well-known that with increasing frequency the alternating current is being distributed on a cross-section of metal conductor unequally in depth, concentrating in its subsurface layer in such a way that under ultrahigh frequency the conductivity is carried out by a thin subsurface layer of metal (the 'skin' effect). Several experimental devices were developed and measurements were conducted using very high frequency (from 6 to 250 MHz) and steel wire specimens charged by cathodic hydrogen [30]. The information gained about H distribution in steel cathodes is in close conformity with the results of anodic dissolution.

References

[1] S.M. Beloglazow, Hydrogenation of Steel During Electrochemical Processes, Leningrad University Press, Leningrad, 1975.
[2] P. Bardenheuer, H. Ploum, MKW Inst. Eisenforsch. 16 (11) (1934) 257–260.
[3] W. Raczynsky, M. Smialowski, Bull. Acad. Pol. Sci., Ser. Sci. Chim. 8 (1960) 209.
[4] B. Baranowski, Z. Szzzklarska-Smialowska, M. Smialowski, Bull. Acad. Pol. Sci., Ser. Sci. Chim., Geolog., Geogr. 6 (1958) 179.
[5] R.P. Fromberg, W.J. Barnett, A.R. Troiano, Trans. Am. Soc. Mater. 47 (1955) 892.
[6] T. Toch, W. Boldwin, in: Corrosion, Embrittlement and Fracture, Metallurgizdat, Moscow, 1961, p. 166.
[7] S.M. Beloglazow, Fiz. Met. Metalloved. 15 (1963) 885.
[8] S.M. Beloglazow, The Hydrogen distribution during cathodic metal, in: S.M. Beloglazow (Ed.), Hydrogenation of Metal During Electrochemical Processes, Leningrad University Press, Leningrad, 1974, p. 10.
[9] H.R. Heat, J. Appl. Phys. 3 (1952) 13.
[10] W. Raczynsky, Archiv Hutnictwa 3 (1958) 19.
[11] P. Bardenheuer, H. Ploum, MKW. Inst. Eisenforsch. 16 (1934) 129.
[12] M. Smialowski, Wodor W Stali, Wydawnictwa naukowo techniczne, Warszawa, 1961.
[13] S.M. Beloglazov, Zavodskaya laboratoria 26 (1961) 1047.
[14] S.M. Beloglazov, T.I. Balvochene, Fiz.-Khim. Mehan. Materialov 22 (4) (1987) 113.
[15] S.M. Beloglazov, V.P. Poljudova, Fiz.-Khim. Mehan. Materialov 16 (1981) 17.
[16] S.M. Beloglazov, I.A. Ermakova, I.V. Kosyrikhina, Praktika Protivokorrozionnoj Zaschity 4 (14) (1999) 52.
[17] I.V. Kosyrikhina, I.A. Ermakova, S.M. Beloglazov, in: 50th ISE Meeting, Pavia, 1999, Ext. Abstr. 835.
[18] S.M. Beloglazov, I.A. Ermakova, I.V. Kosyrikhina, in: Proc. EUROCORR 99, Aachen, 1999, p. 230.
[19] S.M. Beloglazov, K.V. Egorova, N.V. Kolesnikova, in: Interfinish, 15th World Congress, Garmisch-Partenkirchen, 2000, p. 131.
[20] V.A. Slezhkin, S.M. Beloglazov, in: 15th World Congress, Garmisch-Partenkirchen, 2000, p. 162.
[21] S.M. Beloglazov, T.B. Postnikova, E.V. Frolova, Fiz.-Khim. Mehan. Materialov 21 (6) (1986) 108.
[22] S.M. Beloglazov, I.A. Ermakova, I.V. Kosyrikhina, in: Microbial Corrosion, EFC Publ. No. 29, London, 2000, p. 232.
[23] Z.I. Jafarov, S.M. Beloglazov et al., Fiz.-Khim. Mehan. Materialov 36 (4) (1990) 38.
[24] G.S. Beloglazov, S.M. Beloglazov, Proc. 8th Eur. Symp. Corr. Inh. (8 SEIC), Ann. Univ. Ferrara, N.S., Sez. V, 10 (Suppl.) (1995) 1251.
[25] A.A. Myamina, S.M. Beloglazov, in: Proc. EUROCORR 99, Aachen, 1999, p. 231.
[26] A.A. Myamina, S.M. Beloglazov, in: The 2nd Int. Conf. Basic Sci. Adv. Technol., Assiut, 2000, p. 187, Abstr. (III-A) M8.
[27] S.M. Beloglazov, A.A. Myamina, E.M. Kondrasheva, Y.V. Goliak, in: 15th World Congress, Garmisch-Partenkirchen, 2000, p. 143.
[28] K. Kamachi, T. Mutsumi, J. Jpn. Inst. Metals 40 (1976) 821.
[29] R.A. Ryabov, L.M. Syrych, E.S. Kodes, P.V. Geld, Izv. Vuzov Chernye Metally 5 (1974) 128.
[30] S.M. Beloglazow, L.K. Yagunova, E.G. Yagunova, Corrosion in natural and industrial environment. Problems and solutions, in: Proc. Int. Conf. Grado, 1995, p. 319.
[31] S.M. Beloglazow, L.K. Yagunova, Protection Cathodique et Revetements Associes, EFC-CEFRACOR, Recueil, 2002, p. 249.