THE ANNALS OF “DUNAREA DE JOS” UNIVERSITY OF GALATI.
FASCICLE IX. METALLURGY AND MATERIALS SCIENCE
N^{0}. 2 – 2009, ISSN 1453 – 083X

RESEARCHES ON THE CORROSION BEHAVIOR FOR A DRAWING STEEL THAT WENT THROUGH NATURAL AGEING

Florentina POTECAŞU, Octavian POTECAŞU,
Elena IONIŢĂ, Alina CIUBOTARIU
Dunărea de Jos University of Galaţi
email: fpotec@ugal.ro

ABSTRACT

The paper presents the results of a study on the corrosion behaviour of the sheets of drawing steel with 0,04% C gone through natural ageing and run for a period of 112 days from the moment of drawing. The researches highlighted the fact that the phenomenon of natural ageing speeds up the corrosion process. As a result the durability of the products realized from sheet and straps of steel depend also on the protection of their surfaces through different coating procedures.

KEYWORDS: corrosion behaviour, drawing steel, natural ageing, structure

1. Introduction

By drawing there is executed a wide range of marks, very varied as shape and dimensions that are a component of the resistance structure, as well as in elements of car bodies. This drawn marks, simple or complex, require that the used semiproducts to satisfy certain conditions referring to the physical and mechanical characteristics, durability, accessibility, low price, good workability, etc. The usage of steels in the car industry is conditioned to accessibility, low price, good workability besides the mechanical and physical characteristics.

The running conditions often make the environment be a factor that determines an increase to corrosion and a decrease of the lifetime of the marks obtained through the plastic deformation of the steel sheets.

The chemical composition and the main mechanical characteristics of the chosen steel for the study of the corrosion behaviour are presented in table 1 according to STAS SR EN10030.

Table 1. *The chemical composition of the steel*

Steel	**C**	**Mn**	**Si**	**P**	**S**	**Al**	**Cu**	**Cr**	**Ni**	**V**	**Mo**	**Ti**
	[%]											
DC04-A	0.040	0.3000	0.025	0.015	0.010	0.068	0.020	0.010	0.020	0.004	0.003	0.005

Table 2. *The mechanical characteristics of the steel*

The breaking strength, Rm	**The yield point, Rp0.2**	**The elongation strength, An**	**The Erichsen parameter, IE**	**The anisotropy coefficient, r_{90}**	**The cold-hardening coefficient, n**
[N/mm^2]		[%]	[mm]		
270-370	max 210	min 30	min 8.90	min 1.6	min 0.18

The corrosion resistance, or the chemical stability, is the metallic materials’ property to oppose to the destructive action of the atmospheric and chemical agents, called corrosion.

When the corrosive environment is an electrolyte (environment with dissociated ions capable to get metal ions), the corrosion is an electrochemical process. The corrosion is manifested by the loss of weight, the structure change, the chemical composition, the dimensions, the surface colours and the physical, mechanical and technological properties of the metallic materials.

In fact, all the metallic materials in the presence of oxygen get oxidized, but their resistance to oxidation and corrosion depend on the oxide film quality formed at the surface. When the oxide film is compact, thin and adherent to the metal, this isolates the metal from the corrosive agent, and the corrosion resistance of this one is high (the case of platinum, iridium, gold, copper, silver, wolfram, zinc, lead, nickel, crom, molibden, titanium, etc., that normally do not corrodate). The phenomenon is called metal passivisation. When the oxide film is spongy and nonadherent to the material, this allows permanent contact between the material and the chemical agent, and the corrosion phenomenon continues up to the complete elimination, as it is the case for iron and its common alloys with Carbon – steels and pig irons.

The degradation after the interaction with the environment can be the result of a general corrosion or by pitting corrosion [1, 2].

One can notice that the pitting corrosion is one of the major mechanisms that affect the integrity of the marine structures. As a rule, the pitting corrosion is initiated due to some physical and chemical heterogeneousness [3] on the metal’s surface, determined by inclusions, secondary phases, flaws, mechanical degradation.

It is known that the pitting corrosion has a special effect on the fatigue resistance. The fatigue flaws are usually initiated from the zones with pitting degradations [4]. As a result of the interaction between the cyclic stress and the corrosive environment, the cyclic stress favours the pitting process, and the pitting corrosion, as a form of some geometrical discontinuity, leads to the nucleation and later on to the spread of flaws [5].

The concomitant action of mechanical stresses and aggressive environment lead to the degradation of the element areas made of steel or other metallic materials, a process called corrosion under tension and in case of variable stresses - corrosion fatigue, which have different causes and effects as compared to the degradation under the single action of either mechanical stresses or corrosive environment.

The evolution rate of the corrosion under stress and the fatigue process in corrosive environment (fatigue corrosion) is much higher than the two processes considered separately and their effect is not additive (simple overlapping of individual effects), but much more complex.

The complex interaction of the mechanical and chemical factors is highlighted by the fact that the phenomenon of corrosion under stress and the fatigue corrosion can occur in weakly corrosive chemical environments and the mechanical stress producing the process is of low levels, below the material yielding point, in some cases representing only a fraction of its value.

According to the electrochemical theory [11], the occurrence of cracks in the metal under the concomitant action of the corrosive environment and the mechanical stresses is a predominantly electrochemical process and is related to the localization of the corrosion process in various areas of the deformed metal. These areas are considered of high sensitivity for the production of anodic dissolution processes. They are usually located on the border of the crystalline grains and facilitate destruction by intercrystalline corrosion [12]. Thus, the large group of carbon steels and alloys based on aluminium can be destroyed through such a mechanism [13]. However, the sensitivity of these alloys to intercrystaline corrosion is not a sufficient condition for destruction by corrosion under stress. There are such cases when the destruction takes place due to intercrystalline corrosion. This phenomenon is related to the fine structure of the deformed metal. In metals, due to mechanical stresses, the dislocation movement is based on their plane accumulation; they tend to decay by trans-crystalline corrosion, while those with the cell structure dislocations are mainly destroyed by inter-crystalline corrosion.

In metals where there are no local areas favouring dissolution, dislocation migration occurs due to mechanical stresses. In these metals process localization takes place because of the rupture of the protective oxide films [14], which will lead to the formation of new anodic areas, the other areas forming the cathode.

Research [15, 16] has shown that flaws may occur on metal surfaces in those places where the slip bands exit which further result in formation of small pits.

2. Determinations and experimental results

2.1. The evaluation of the corrosion resistance of the steel sheets

In figure 2 it is presented the microstructure of the blank assay before going through corrosion.

Fig. 1. *The surface aspect of the blank assay x200 (before the corrosion)*

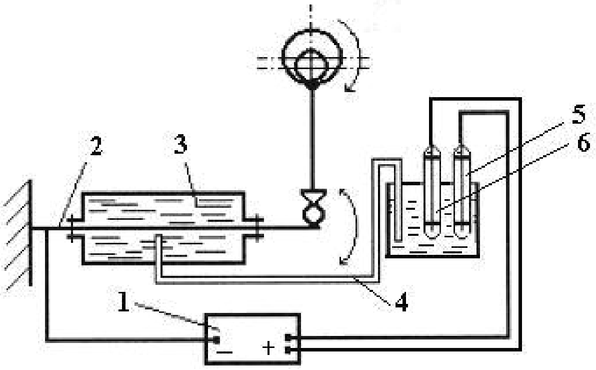

Fig. 2. *Potentiometer device:1 – PGP 201 Potentiostat; 2 – working electrod (WE); 3 – the sollution of 3.5% NaCl; 4 – bridges of salt; 5 – auxiliary electrod (CE); 6 – refernce electrod (RE)*

By means of a potentiometers device (fig. 3) consisting of a PGZ100 All-in-one Potentiostat (1), a saturated calomel electrode as reference electrode (6), a platinum electrode as auxiliary electrode (5) and a sample as working electrode (2), was recorded in situ, the evolution of the electrode potential after the cold plastic deformation and after the natural ageing run for a period of 5 months.

The system was connected to a computer with data analysis software. The samples to be analysed (the working electrode) were isolated at one end before the immersion in the testing solution 0,5N NaCl. The corrosion tests of each sample began with monitoring the corrosion potential (open circuit potential – OCP) after the sample immersion in the testing solution until this **reached the stationary values.**

Seven determinations were made in ≈ 30 minutes and the following results from the table 3 graphically represented in fig. 3 were obtained:

Table 3. *The evaluation of the corrosion resistance of the steel sheets*

	Sample surface	Rp	Calculated Rp t	The corrosion speed	The calculated corrosion speed
	[cm^2]	[Ωxcm^2]		[μm/an]	
1	1.8	292.1	525.78	486.3	875.34
2	1.8	321.4	578.52	441.9	795.42
3	1.8	308.2	554.76	460.9	829.62
4	1.8	344.3	619.74	412.6	742.68
5	1.8	333.2	599.76	426.3	767.34
6	1.8	317.5	571.5	447.4	805.32
7	1.8	203.0	365.4	699.6	1259.28

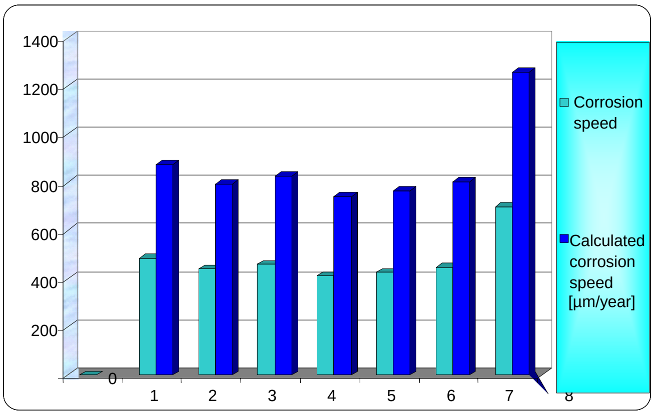

Fig. 3. *The corrosion speed of the steel sheets before the natural ageing*

In figure 4 are presented macrostructural aspects from the surface of the steel samples after three weeks of natural ageing after having been exposed to corrosion.

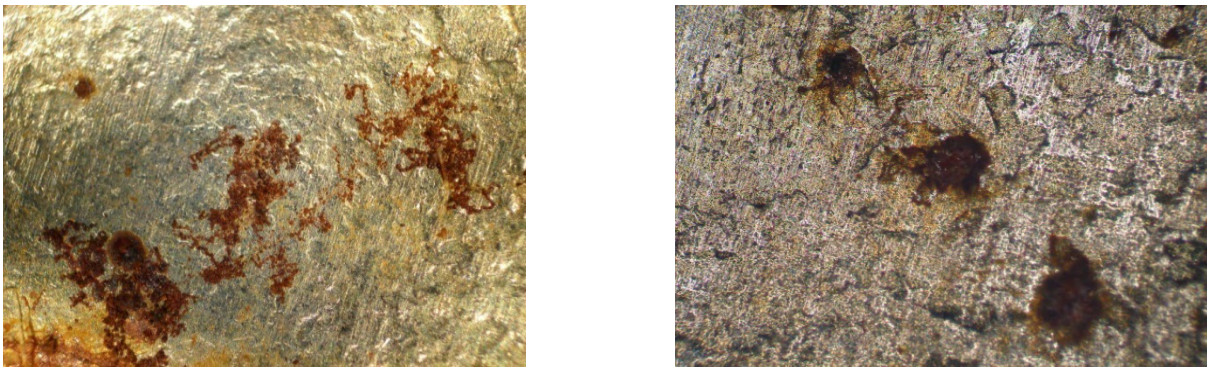

Figure 4 *The macrostructural aspects of the surface of the steel samples after three weeks of natural ageing, exposed to corrosion; x 100*

After 112 days other determinations of speed corrosion were made in order to observe the differences owed to the process of natural ageing. The corrosion tests began by monitoring the corrosion potential (open circuit potential – OCP) after the sample immersion in the testing solution until it reached the stationary value. In table 4 and fig. 5 are presented the obtained results.

Table 4. *The evaluation of the corrosion resistance of the steel sheets (after112 days)*

	The sample surface	**Rp**	**Calculated Rp**
	[cm^2]	[Ωxcm^2]	
1	1.2	519.663	623.596
2	1.2	539.075	646.890
3	1.2	525.210	630.252
4	1.2	466.697	560.036
5	1.2	476.953	572.344
6	1.2	494.408	593.290
7	1.2	415.654	498.785

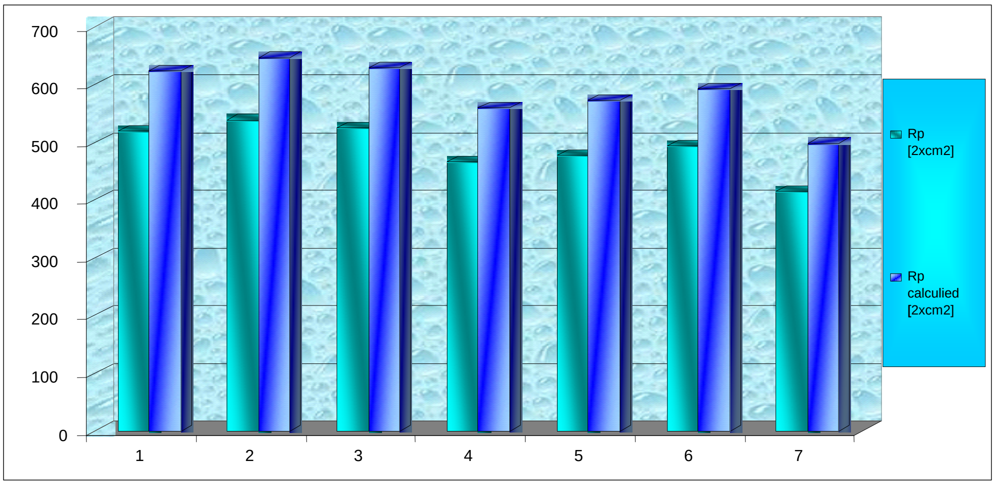

Fig. 5. *The polarization resistance of the steel sheets exposed to natural ageing for 112 days.*

In figure 6 it is presented the evolution of the electrode potential for the two situations – before and after the natural ageing of the steel sheets. As one can notice, the phenomenon of natural ageing leads to moving the potential of electrode towards the more electronegative anodic zone.

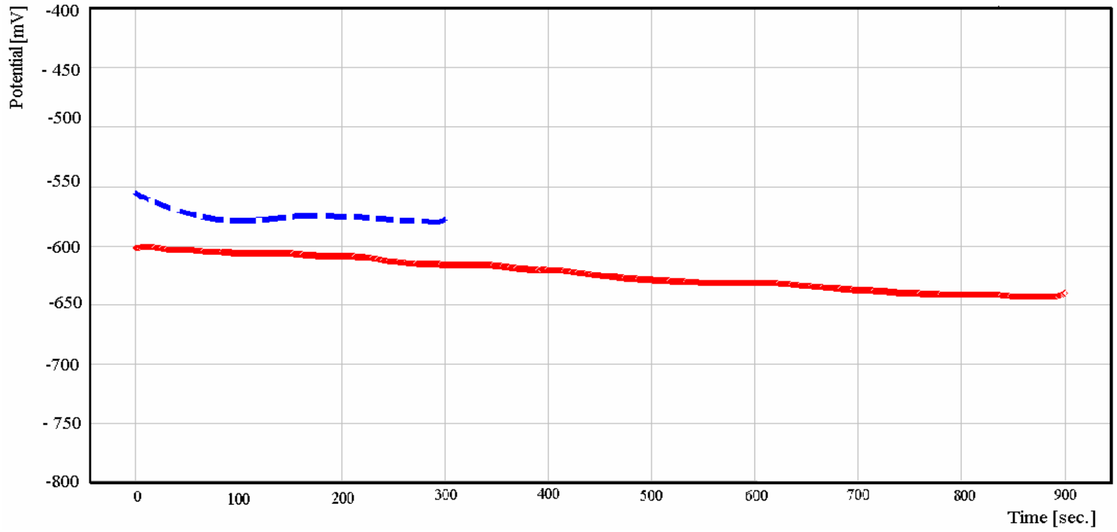

Fig. 6. *The evolution of the electrode potential [mv] in time [seconds] for the steel sheet before (- - -) and after corrosion (——)*

In fig. 7 it is presented the macrostructural aspect of the samples exposed to corrosion after 112 days of natural ageing.

One can notice a noticeable evolution of the corrosion mechanisms.

The corrosion is realized mainly by pitting and in other zones it developed a local corrosion on surfaces identified through the red colour, due to the elimination of a brown-red powder of iron oxide (Fe_2O_3 hard and Fe_3O_4).

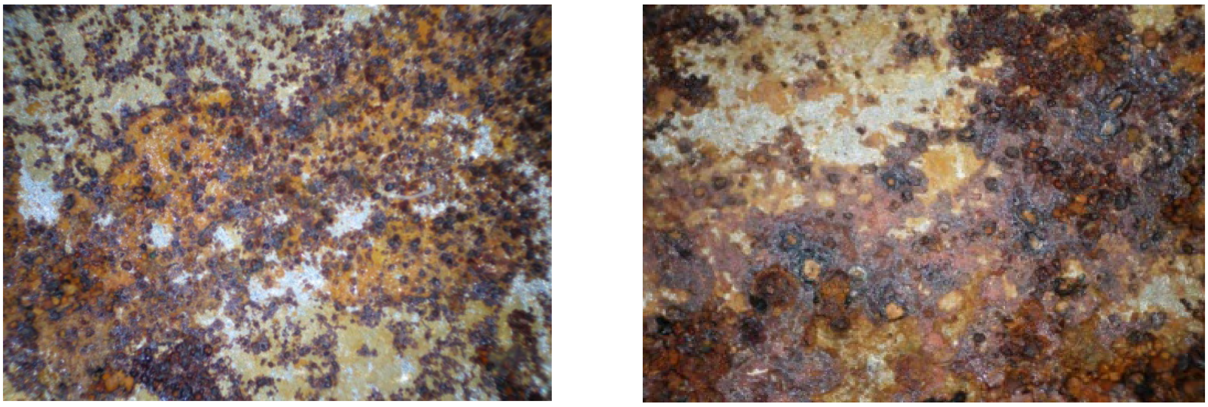

Fig. 7 *.The macrostructural aspects of the steel sample surface exposed to corrosion, after 112 days of natural ageing, x 100*

3. Conclusions

- The research made on the corrosion behaviour of the steel intended for drawing, showed that the phenomenon of natural ageing speeds up the corrosion process.
- Thus, it was highlighted the correlation between the polarization resistance and the corrosion speed. The higher the polarization resistance, the lower the corrosion speed. The samples naturally aged for a period of 112 days presented a much lower polarization speed as compared to the behaviour between the ageing; the polarization resistance is 1,7 times lower and the speed corrosion is much increased by 2,5 times, which requires a very strict control of the coating for the table protection with the objective of increasing the product's lifetime.
- In the tests of accelerated corrosion, we noticed that the main mechanisms of corrosion are the pitting and the local corrosion on zones identified by the red colour due to the elimination of a brown-red powder of iron oxide (Fe_2O_3 hard and Fe_3O_4).
- When exploiting it is necessary to use the covered sheets (with compact films, adherent, without flaws) for increasing the corrosion resistance and the exploiting durability.

References

[1]. Melchers, R. - *The effect of corrosion on the structural reliability of steel offshore structures.* Corrosion Science, 47, 2005, pp. 2391–2410

[2]. Vasudevan, A.K., Sadananda, K. - *Classification of environmentally assisted fatigue crack growth behaviour.* International Journal of Fatigue, doi: 10.1016/j. ijfatigue.2009.03.019.

[3]. Pidaparti, R.M., Rao, A.S. - *Analysis of pits induced stress due to metal corrosion*. Corrosion Science, 50, 2008, pp. 1932-1938

[4]. Rokhlin, Kim, J.Y., Nagy, H., Zoofman, B. - *Effect of pitting corrosion on fatigue crack initiation and fatigue life*. Engineering Fracture Mechanics 2, 1999, pp. 425-444

[5]. Pidaparti, R.M., Potel, R.R. - *Correlation between corrosion pits and stresses in Al alloys,* Material Letters, 67, 2008, pp. 4497-4499

[6]. Hoeppner, **D.W**. - *Fatigue mechanisms*. STP, vol.67, American Society for Testing and Materials, Philadelphia, PA, 1979, pp.841

[7]. Goswami, K., Hoeppner, D.W. - *Pitting corrosion fatigue of structural materials*. Structural integrity in aging aircraft. New York: ASME, 1995, pp. 129-139

[8]. Bastidas-Arteaga, E., Bressolette, P., Chateauneuf, A., Sanchez-Silva, M. - *Probabilistic lifetime assessment of RC structures under coupled corrosion-fatigue deterioration processes*. Structural Safety, 31, 2009, pp.84-96

[9]. Sivaprasad, S., Tarafader, S., Ranganeth, V.R., Tarafader, M, Ray, K.K. - *Corrosion fatigue crack grawth behaviour of naval steels*. Corrosion Science, 48, 2006, 1996 – 2013

[10]. Poursace, A., Hansson, C.M. - *Potential pit falls in assessing chloride-induced corrosion of steel in concrete***.** Cement and Concrete Researche, doi:10.1016/j.cemconres.2009.01.015.

[11]. Hoar, T.P., Hines, J.G. - In: Jour. Iron Steel Inst.vol.5, 1956, p.124,

[12]. Arafin, M.A., Spunzar, J.A. - *A new understanding of intergranular stress corrosion cracking resistence of pipeline steel through grain boundary character and krystallographie texture studies*. Corrosion Science, 51, 2009, pp. 119-128.

[13]. Olache, O.B., Zaro, S.A., Okafor, E.G. - *Analytical correlation between varying corrosion parameters and corrosion rate of Al-4.5Cu/10%ZrSiO$_4$ composite in hydrochloric acid by rate rare earth chloride*. Journal of Alloys and Compounds, 2009, 472, pp. 178-185.

[14]. Hall Jr, M.M. - *Film rupture model for aqueous stress corrosion cracking under constant and variable stress intensity factor,* Corrosion Science, doi: 10.1016/j.cor.sci.2008.08.052.

[15]. Nielson, N.A. - *Nature of initial corrosion of stressed austenitic steel by chloride ions*. In: Corrosion, vol.20, No.4, 1964, pp.104-112.

[16]. Jones, R.L. - *Potential and chloride effects in the stress corrosion cracking of type 304 stainless steel in 290^{o}C water*. In: Corrosion, vol.31, No.12, 1975, pp. 424-431.