

MÖSSBAUER EFFECT INVESTIGATION OF FE-C STEEL ELECTROLYTIC GALVANISATION

Ion BIBICU^{1,2}, Caius BULEA³, Vasile RUS³

¹Full Member of the Academy of Technical Sciences in Romania

²National Institute of Materials Physics, Bucharest-Magurele,

³SC BETAK SA, Bistrita-Nasaud

Abstract Galvanizing is a very well known industrial process for anticorrosive and protection coatings. At first sight, galvanizing should not need any further important research and development involvement but many reasons contradict this appreciation: the constant emergence of new sophisticated steel grades, the sustainable requirement of strictly controlled microstructure, new designed surface treatment, etc. There are, relatively, few studies dedicated to electrogalvanizing, most of these are dedicated to hot-dip galvanizing. The Mossbauer effect allows nondestructive superficial studies for iron compounds and remains today as the only technique to reliably monitor *in situ* the Fe-Zn phase composition from the interface steel-zinc coating. Samples of industrial Fe-C steel with low C concentrations (up to 0.04 wt. %) were electrogalvanized. We were interested mainly to investigate the influence of the sample preparation procedure before galvanization and the interface between steel and Zn coating. It is possible to obtain new information about mechanism and the kinetics of the coating formation. The Mossbauer measurements were performed in two geometries: transmission and backscattering. By transmission geometry, which imply a sample preparation, were obtained sample volume information. By backscattering geometry, which do not imply sample preparation, were obtained surface data before and after electrogalvanizing. Surface measurements were realized by detection of conversion electron (CEMS) and conversion X-ray (CXMS). The maximum studied depths are: 200 nanometres by conversion electrons and 20 microns by X-rays. The CEMS spectra of the sample prepared for deposition reveals a magnetic anisotropy: a preferred direction of the magnetic moments of the iron nuclei. By contrast the transmission spectra and the CXMS spectra (with an exception) show that the magnetic moments inside the sample are practically in a random arrangement. CEMS spectrum for a sample shows the presence of an additional compound without magnetic ordering where Fe has +3 valence. CXMS spectra of the interface are very close to that obtained before galvanizing and do not put in evidence a new compound at interface steel-Zn coating

Keywords: low carbon steel, electrolytic galvanization, Mössbauer effect

1. INTRODUCTION

A Galvanization is a very well known industrial process for anticorrosive and protection coatings [1 – 6]. At first sight, which should not need any further important R & D (research and development) investments in this field. Many reasons contradict this appreciation, among which the constant emergence of new sophisticated steel grades, the sustainable requirement of strictly controlled microstructure, the lightening of structures accompanied by well designed surface treatment, the continuous innovation in the field of fabrication machinery etc. The main industrial processes are hot-dip galvanizing which is based on the reaction of liquid zinc with steel, and the formation of intermetallic compounds (IMCs) and η -Zinc. Electrogalvanized steel is being used increasingly for the manufacture of automobiles, domestic appliances, buildings and other products. There are few studies, relatively; dedicated to electrogalvanized process, the great majority is dealing with hot-dip galvanizing. Recent papers devoted to electrogalvanized process show another structure of the Zn coating without Fe-Zn intermetallic compounds presence [7-9]. Galvannealed coatings are generally about 10 μm (especially electrogalvanized coatings) thick which is ideal for study by transmission and scattering Mössbauer spectroscopy. The scattering geometry permits in-situ analysis

with the coating adhered to the steel. The data as obtained are unable to be determined by commonly used industrial methods such as X-ray diffraction, X-ray fluorescence, electron microscopy and wet chemistry. The Mössbauer effect remains today as the only technique to reliably monitor the Fe–Zn phase composition in galvanized steel [10].

Mössbauer spectroscopy [11] is based on the incorporation of the emitting and absorbing nuclei within a solid matrix, which enables resonant recoil free absorption and emission of γ -rays. Its importance lies in the very narrow line width of the emitting photon resulting from the relatively long lifetime of the excited nuclear state - typically of 10^{-8} s, corresponding to a natural line width of the order of 10^{-8} eV - and the consequent ability to probe the variations in nuclear energy levels resulting from any discrete changes in the chemical state and/or environment of the Mössbauer nucleus [12], [13], [14]. Such changes in nuclear energy levels are measured by modifying the energy of the probing γ -rays by applying a Doppler shift: a Mössbauer spectrum therefore consists of a plot of counts against applied Doppler velocity (positive and negative), the velocities corresponding to the addition and subtraction of Doppler energy shifts to the γ -ray energy. Room temperature measurements can be made on the following isotopes: ^{57}Fe , ^{119}Sn and ^{151}Eu . The ^{57}Fe is the most studied isotope followed by ^{119}Sn and ^{151}Eu . Following resonant absorption of a gamma ray, the nucleus may de-excite by emission of a gamma ray or by the process of internal conversion where an inner shell electron is emitted. Accompanying conversion electron emission, a characteristic X-ray is emitted as a result of the repopulating of the inner energy levels. Detection of the three backscattered particles permits surface studies to be performed at various depths. The smallest depths can be investigated by electron emission.

The main purpose of our measurements was to investigate the influence of the sample preparation procedure before galvanization and the interface between steel and Zn coating. It is possible to obtain new information about mechanism and the kinetics of the coating formation. Samples from low alloyed Fe-C steel were prepared by electrogalvanization at Betak Company, located in Bistrita. BETAK S.A. is a market leader in the production of galvanized steel strips, one of the leading manufacturers of safety guard rails in Romania, manufacturer of various steel structures and supplier of corrosion protection services by hot dip galvanizing and electrogalvanization. Scientific activity is a priority of the SC BETAK SA, and corrosion related phenomena are dealt with responsibility and professionalism. Betak products, facilities and devices employed in their execution, and some of the technologies that are applied in the production process are OSIM registered as patents, brands or designs. This research is in context of collaboration between industry, research and academic units to elaborate new technologies, performing and multifunctional materials, innovative services.

2. EXPERIMENTAL

The electrodeposition of Zn was performed in an electroplating cell of two electrodes. Chemical reagents used are zinc chloride (75g/l), potassium chloride (220g/l), boric acid (23g/l). All the chemicals were of analytic grade and solutions were prepared using deionized water.

Chemical composition in wt% of steel samples was: carbon 0,04%, manganese 0,37%, silicon 0,009%, phosphorus 0,009%, sulphur 0,008%, aluminium 0,035%, copper 0,03%, chromium 0,02%, nickel 0,01%, titanium 0,001%, nitrogen 0,005 %. The samples were obtained from hot laminated roll. Before electroplating commences, steel was degreased, washed with water, descaled and washed with water. Initial sample, sample ready for electrodeposition and electrodeposited sample were measured.

Mössbauer effect measurements were performed in two geometries: transmission and backscattering. By transmission geometry were obtained volume information for the studied samples. A sample preparation procedure was used for measurements in transmission geometry. Thus, a powder with granulation smaller than 0.1 mm was obtained from initial sample and this was used for measurement. Information about samples surfaces, before and after galvanization was found by

backscattering geometry. Backscattering measurements did not include a sample preparation. These measurements were realized by detecting conversion electrons or conversion X-rays. The electrons penetration depth is of the order of 200 nanometers and X-rays penetration depth is of the order of 20 microns [μm]. The backscattering measurements were conducted at a high degree of accuracy with a new detector, gas-flow proportional developed in our institute [15]. This detector is a multi-purpose one; changing detection gas and detection volume it is possible to detect electrons or X-rays. The samples for XRMS measurements were covered with aluminized mylar with 2,5 μm thickness to eliminate conversion electron signal [16]. The K-conversion electrons emitted by the sample are too are detected in X-rays energy range and contribute approximately 20% to the overall signal [16]. Backscattering determinations are more difficult than transmission determinations and in the world there are few places where its can be performed usually.

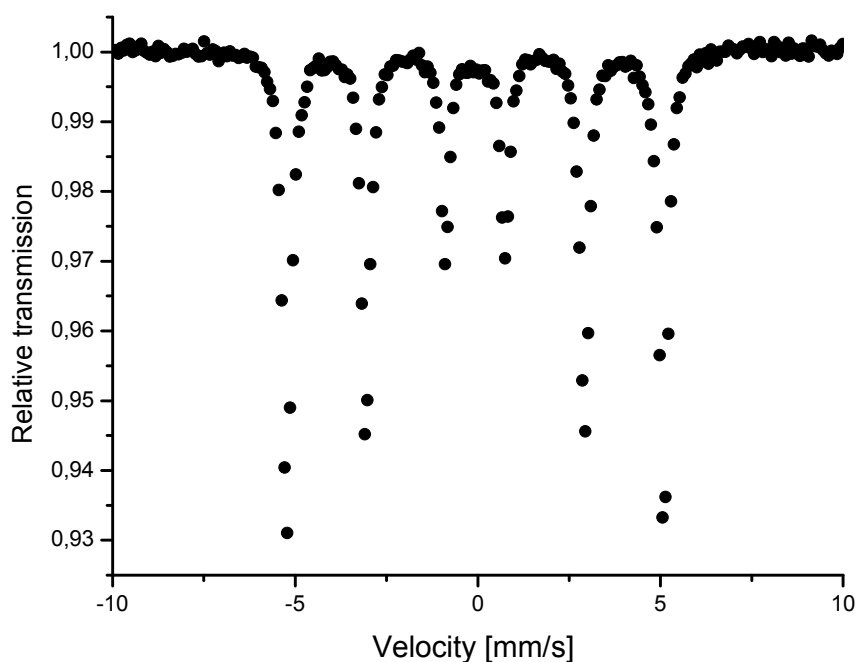


Fig. 1. Mössbauer transmission spectrum of initial sample.

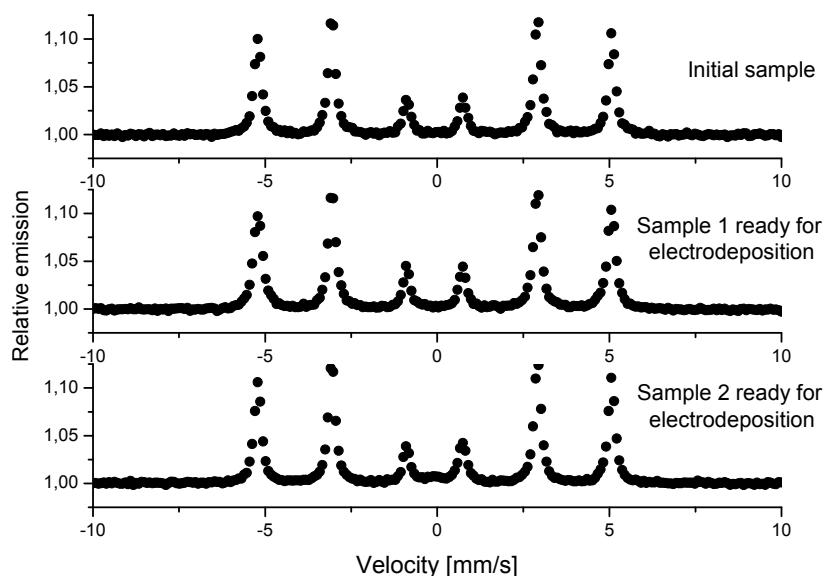


Fig. 2a. Mössbauer spectra obtained by conversion electrons (CEMS) for studied samples (spectra integral plotting).

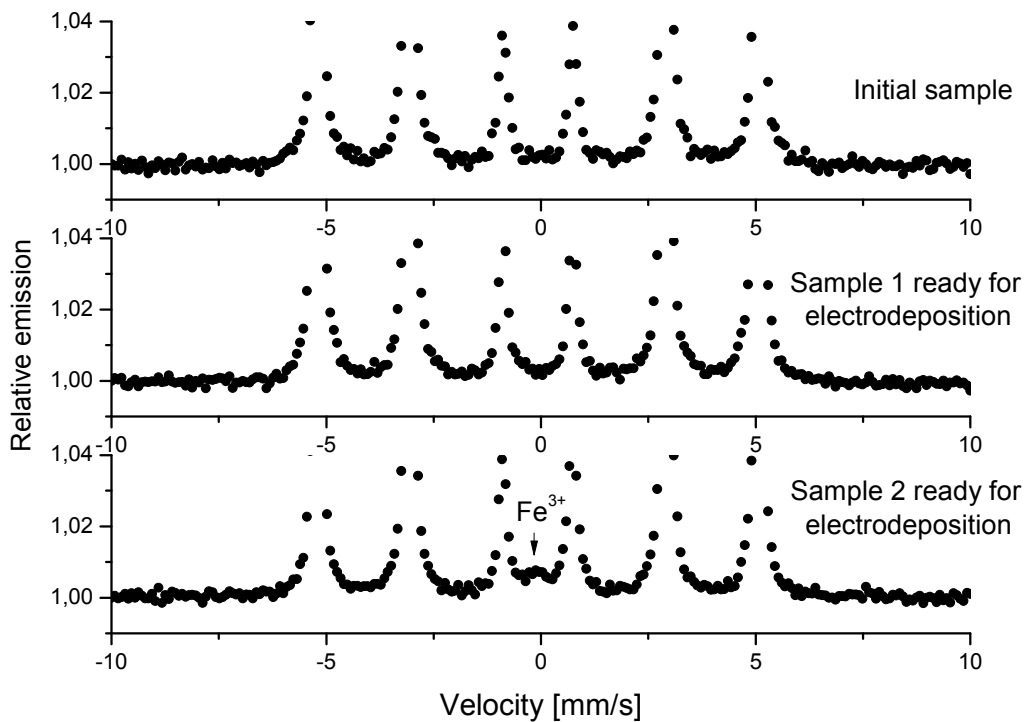


Fig. 2b. Mössbauer spectra obtained by conversion electrons (CEMS) for studied samples (spectra integral plotting at small effect).

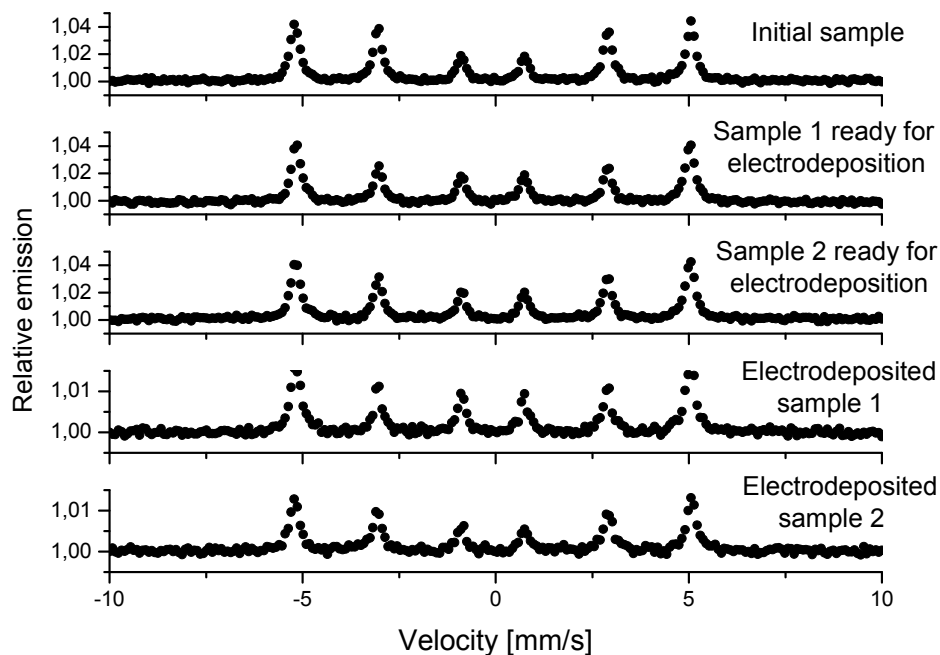


Fig. 3. Mössbauer spectra obtained by conversion X-rays (CXMS) for studied samples.

All Mössbauer measurements were performed at room temperature in the velocity ranges $v \in [-10 \text{ mm/s} \div +10 \text{ mm/s}]$ and $v \in [-2 \text{ mm/s} \div +2 \text{ mm/s}]$, using AME-50 Elscint conventional constant-acceleration spectrometer, equipped with CMCA-550 acquisition module. A ^{57}Co radioactive source, in rhodium matrix and activity around 20mCi was used. The velocity calibration has been performed using $\alpha\text{-Fe}$ standard. The lower velocity range was used for better detection of compounds from interface layer: steel – Zn coating; compounds possibly similar to compounds found in hot-dip galvanizing [10].

3. RESULTS AND DISCUSSION

The obtained spectra are shown in figures 1-4. The parameters of the Mössbauer spectra, for the velocity range $v \in [-10 \text{ mm/s} \div +10 \text{ mm/s}]$, were calculated using a computer fitting program, in the hypothesis of Lorentzian line shape. The spectra were fitted with a single sextet due low carbon content [17], [18], [19]. We added a single line to sextet in one case. Isomer shift values are referred to that of α -Fe.

The parameters of the sextets obtained by spectra fitting are presented in table 1. A central line with a relative area at sensibility limit of the method was added for a CEMS spectrum. The sextets have hyperfine parameters, practically the same as for a α -Fe sample [18 -20]. The variations of its value compared with of the iron field ($H = 330 \text{ kOe}$) is probably related to the plastically-deformed structure accompanying rolling. The rolling procedure leads to elastic displacements from normal lattice sites of some iron atoms [20].

Table 1. The values of the hyperfine parameters obtained from spectra

Sample	Spectrum type	H [kG]	IS [mm/s]	QS [mm/s]	W [mm/s]	A [%]	Line intensity ratio for sextet
Initial sample	TMS	331,4	0,00	0,00	0,28	100	3:2,33:1,26
Initial sample	CEMS	330,1	0,00	0,00	0,27	100	3:3,42:1,10
Sample 1 ready for electrodeposition	CEMS	329,9	0,00	0,00	0,27	100	3:3,16:1,12
Sample 2 ready for electrodeposition	CEMS	332,2 -	0,00 0,01	0,00	0,27 0,39	98,4 1,6	3:3,44:1,21
Initial sample	CXMS	329,3	0,00	0,00	0,27	100	3:2,55:1,28
Sample 1 ready for electrodeposition	CXMS	330,6	0,00	0,00	0,28	100	3:1,60:1,23
Sample 2 ready for electrodeposition	CXMS	332,3	0,00	0,00	0,27	100	3:2,58:1,28
Electrodeposited sample 1	CXMS	332,5	0,00	0,00	0,30	100	3:1,55:1,24
Electrodeposited sample 2	CXMS	331,3	-0,00	0,01 ?	0,29	100	3:2,24:1,19

In the table above: H: magnetic hyperfine field at ^{57}Fe nucleus; IS: isomer shift relative to α -Fe; QS: quadrupole splitting; W: line width; A: subspectrum relative area.

The errors for obtained data are: H: ± 3 ; IS: $\pm 0,02$; QS: $\pm 0,03$; W: $\pm 0,02$; A: ± 3 .

In CEMS spectra (figure 2), the intensities of the second and fifth peaks of these sextets with respect to the third and fourth peaks showed that the directions of the γ -ray and magnetic moments were nearly perpendicular and thus indicate a magnetic anisotropy at surface samples. The magnetic moments of iron tend to be orientated in surface plane. By contrast, the TMS and CXMS (with an exception) showed that the magnetic moments inside the sample were in a random arrangement. The anisotropy found in superficial layer of 200 nm thickness, by CEMS spectra, is mainly obtained in metalurgical process of steel sheets prepared for galvanization. The specific tratment applied before electroplating did not affect the superficial anisotropy. In one sample prepared for electrodeposition we found broader additional line, its presence being at sensitivity limit of the method. The line parameters indicated the presence of an amorphous Fe^{3+} oxide. This compound may be a rest of the oxides formed on the surface during metalurgical process of the steel sheets preparation or it appeared on surface in the time interval between specific tratment before electrodepostion and Mössbauer measurement moment.

The parameters of CXMS spectra are similarly to that obtained for TMS spectra with one single exception: sample 1 ready for electrodeposition. There is an magnetic anisotropy in superficial layer with 20 microns thickness for this sample. The anisotropy is opposite to that found by CEMS spectra:

the directions of the γ -ray and magnetic moments were nearly in a parallel direction. The magnetic moments of iron tend to be perpendicularly on sample surface. The metalurgical process of steel sheets preparation is responsible for this anisotropy.

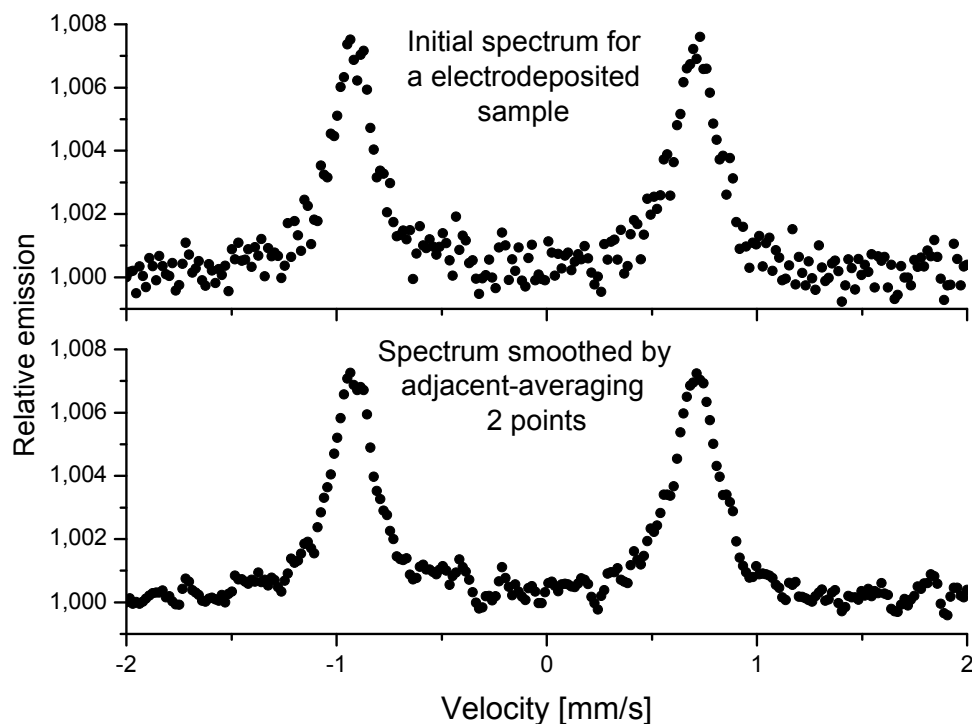


Fig. 4. Mössbauer spectrum obtained by conversion X-rays (CXMS) of electrodeposited sample at lower velocity range.

CXMS spectra of the electrodeposited sample evidenced properly steel substratum and its parameters are practically the same with that obtained before deposition. The spectra did not show the presence of a new compound between steel and Zn coating. For a better information we repeat a CXMS measurement for a electrodeposited sample at lower velocity range (± 2 mm/s) and a doubled statistics. The obtained spectrum and that smoothed by two points adjacent-averaging method are shown in figure 4. The spectra and their fitting did not indicate, again, the presence a new compound in the interface steel-Zn coating. The smothing technique applied to Mössbauer spectra increase signal/noise ratio.

4. CONCLUSIONS

The presence of a new compound in the interface between steel substrate and zinc coating was not detected.

There is a magnetic anisotropy in outer superficial layer (200 nm thickness): the iron magnetic moments are oriented preferentially in surface sample. A magnetic anisotropy, opposite to the precedent, can be presently in a thicker surface layer (20 μm): the iron magnetic moments are oriented near perpendicularly to surface sample. The anisotropies are, mainly, due metalurgical process of steel sheets preparation.

It is possible to detect the presence of iron oxides on the surface.

ACKNOWLEDGMENTS

Financial support from the National Authority for Scientific Research (ANCS) (Core Program contract PN09-45) is gratefully acknowledged

REFERENCES

- [1] A. N. Minkevici, *Tratamente termochimice ale metalelor și aliajelor*, Editura Tehnica Bucuresti, 1968.
- [2] O. Kubaschewski, *Iron-Binary Phase Diagrams*, Springer-Verlag, 1982.
- [3] M. Anghel, *Protecția anticorozivă prin zincare termică*, Editura Tehnica Bucuresti, 1992.
- [4] R. G. Grant Ph. D. Thesis, Old Dominion University, 1995, UMI # 9530660.
- [5] Y. De Abreu, A. Da Silva, A. Ruiz, A. Réquiz, N. Angulo, R. Alanis, *Surf. Coat. Techn.* 120-121 (1999) 682-688.
- [6] K. Bai, P. Wu, *J. Alloys Comp.*, 347 (2002) 156-164.
- [7] S. Basavanna, Y. Arthoba Naik, *J Appl Electrochem* 39 (2009) 1975–1982.
- [8] A.P.I Popoola, O.S.I Fayomi and O.M Popoola, *Int. J. Electrochem. Sci.*, 7 (2012) 4860 - 4870.
- [9] O.S.I Fayomi, A.P. I Popoola, *Int. J. Electrochem. Sci.*, 7 (2012) 6555 - 6570.
- [10] D. C. Cook, *Hyperfine Interactions* 141/142 (2002) 21–34.
- [11] R. L. Mössbauer, *Z. Physik*, 151 (1958) 124-143.
- [12] G. J. Long, F. Grandjean, eds., *Moessbauer Spectroscopy Applied to magnetism and Materials Science*, vol 2, Plenum, Dordrecht, 1996.
- [13] A. G. Maddock, *Moessbauer Spectroscopy: Principles and Applications of the Techniques* (Horwood Chemical Science Series), Horwood, Chister, 1997.
- [14] G. N. Belozerskii, *Moessbauer Studies of Surface Layers*, (Studies in Physical and Theoretical Chemistry Series; 81), Elsevier Science, Oxford, 1993.
- [15] I. Bibicu, G. Nicolescu, C. Cretu, *Hyp. Interact.*, 192 (2009) 85-91.
- [16] Laura K. Perry, D. H. Ryan, R. Gagnon, *Hyperfine Interact* 170 (2006) 131–143.
- [17] I. Bibicu, A. Samide, M. Preda, *Materials Letters* 58 (2004) 2650.
- [18] E. Güler, *Materials Chemistry and Physics* 107 (2008) 183.
- [19] Cs. Vertes, M. Lakatos-Varsanyi, W. Meisel, A. Vertes, P. Gütlich, *Nucl. Instr. and Meth. in Phys. Res.* B76 (1993) 20-21.
- [20] F. Z. Bentayeb, B. Bouzabata, S. Alleg, *Hyp. Interact.*, 128 (2000) 375-380 .
- [21] W. Olszewski , K. Szymanński, D. Satuła, L. Dobrzyński, L. Bottyán, F. Tanczikó, *Nuclear Instruments and Methods in Physics Research B* 266 (2008) 3319–3324.

INVESTIGAREA PRIN EFECT MÖSSBAUER A GALVANIZARII ELECTROLITICE A OTELULUI FE-C

Ion BIBICU^{1,2}, Caius BULEA³, Vasile RUS³

¹Membbru titular al Academiei de Științe Tehnice din România

²Institutul National de Cercetare Dezvoltare pentru Fizica Materialelor, Bucuresti-Magurele

³Societatea Comerciala BETAK SA, Bistrita-Nasaud

Rezumat : Galvanizarea este un foarte cunoscut proces industrial pentru acoperiri anticorozive si de protectie. Aparent nu ar fi necesare noi investitii in cercetare pentru acest domeniu dar multi factori contrazic aceasta apreciere: folosirea unor noi tipuri de oteluri, controlul strict al microstructurii, tratamente superficiale sofisticate, etc. Exista relativ putine studii consacrate depunerii electrolitice, majoritatea se ocupa de depunerile termice. Efectul Mossbauer permite efectuarea de studii de suprafata nedestructive ale compusilor de fier si este singura tehnica de monitorizare certa *in situ* a a posibililor compusi Fe-Zn de la interfata otel-depunere de zinc. Probe din otel Fe-C cu un continut scazut de carbon (pana la 0,04% in greutate) au fost galvanizate electrolitic S-a urmarit obtinerea de informatii despre starea suprafetei inainte de galvanizare si despre stratul de interfata dintre otel si depunerea de Zn. Aceste informatii pot ajuta la o mai buna intelegere a mecanismului de formare si a cineticii stratului de acoperire. Masuratorile prin efect Mössbauer s-au realizat in doua geometrii: transmisie si retroimprastiere. Prin geometria de transmisie, care implica o preparare a probei s-au obtinut informatii de volum. Prin geometria de retroimprastiere s-au obtinut informatii asupra suprafetei probelor inainte si dupa procesul de galvanizare. Masuratorile de retroimprastiere, care nu au inclus o pregatire a probelor pentru

obtinerea spectrelor, s-au realizat prin detectia electronilor de conversie (CEMS) si a razelor X de conversie (CXMS). Detectia electronilor de conversie permite obtinerea de informatii din stratul superficial cu o grosime maxima de 200 nanometri iar a razelor X de conversie din stratul stratul superficial cu o grosime maxima de 20 micrometri. Spectrele CEMS arata ca la suprafata probelor pregatite pentru depunere exista o anizotropie magnetica: o orientare preferentiala a momentelor magnetice ale nucleelor de fier. Aceasta anizotropie nu exista in spectrele (CXMS), cu o exceptie sau cele obtinute prin transmisie. Intr-o proba prin spectrul CEMS s-a pus in evidenta si prezenta unui compus superficial, fara ordonare magnetica, in care Fe are valenta +3. Spectrele CXMS ale interfetei sunt apropiate de cele obtinute inainte de acoperire si nu pun in evidenta un compus nou la stratul de interfata proba otel-strat de Zn.