Int. J. Electrochem. Sci., 8 **(2013)** 8291 - 8298

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short Communication

Effect of Additive on the Internal Stress in Galvanic Coatings

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Received: 21 January 2013 / *Accepted:* 28 April 2013 / *Published:* 1 June 2013

The paper deals with determination of internal stress during an electroplating process. The properties of galvanic coatings, such as hardness, adhesion and abrasion resistance, depend also on the magnitude of internal stress. The measurements of stress were carried out on specimens with galvanic coatings deposited to a Ni base without and with an additive. The results of experiments were evaluated in terms of potential relationships.

Keywords: coating, Ni-Co alloy, electrodeposition, stress, IS meter

1. INTRODUCTION

During electroplating process the internal stresses develop in the coat layer. These stresses are conditional on differences in the structure of coating during crystallization, presence of foreign non-metal components from the electrolyte, variability of process parameters and last but not least chemical composition of the electrolyte [1,2].

According to the extent of their action, internal stresses can be divided as follows: macroscopic, microscopic and submicroscopic. Macroscopic stresses originate from inhomogeneities. On the microscopic scale they can, for example, start at grain boundaries, the locations or accumulation of dislocations. Tensile or compressive macroscopic stresses develop in galvanic coatings. The action of internal stresses during depositing of coatings results in oriented resultant strain in the final product [3-6]. Prevailing tensile stresses increase abrasion resistance while predominance of compression stresses increases strength and hardness of the coating. High internal stresses increase brittleness. Another cause of development of stresses in electrodeposited coatings, besides crystallization inhomogeneities, is the electrochemical cathodic hydrogen ion reduction. Under favourable conditions for H^+ ions diffusion, which occur easily due to small size of hydrogen ions, these ions diffuse to active centres in the material. Transformation of ions to hydrogen molecules and the accompanying volume changes give rise to internal stresses. Cathodic reduction of hydrogen can be affected by correct management of the electrochemical process of coating [7-10]. According to [9], the level of internal stress in the coating is influenced particularly by cathodic current density and temperature of the electrolyte.

The reduction in magnitude of stresses during electrodeposition processes has been achieved by electrolyte additives. They may be organic or metal. During the coating process, they are adsorbed to the developing coating and remain its component after crystallization. In addition to reducing the stresses, additives increase lustre of the deposited coatings, reduce growth and thus also the size of crystallites, alter mechanical and physical properties and increase the range of current density of the process. Adsorption properties of the additive are highly effective due to the fact that its relatively low concentrations, mostly at the level of mg/l, can work at the most active sites of the relatively large surface of the developing coating [10-14].

The methods used for determination of internal stresses can be divided to three groups, namely mechanical, magnetic and roentgenographic. The mechanic methods based on a simple principle of measurement of deformation or deformation force allow one to determine the stress during the galvanization process. Men level and character of stresses is determined after depositing the coatings. The magnetic methods are based on the fact that internal stresses in the galvanic coating deposited on material of suitable magnetostriction properties induce in this material tensile or compressive stresses that change its original magnetic properties. The principle of measurement of stresses by roentgenographic methods is based on measurement of changes in the distance of lattice planes. This method can be used only on already deposited coatings after completion of the galvanic process [6-9].

2. EXPERIMENTAL MATERIAL AND EXPERIMENTAL METHODS

The experiments were carried out on a steel band of dimensions 250x13x0.05 mm, Fig. 1. Its upper and lower part was insulated with nitro-varnish so that its length during coating was 180 mm. After drying of the varnish, the ends were finished in order to ensure electric contact between specimen and the IS meter. Galvanic coating took place in an electrolyte. Composition of the electrolyte and technological parameters of the coating process are presented in Table 1.

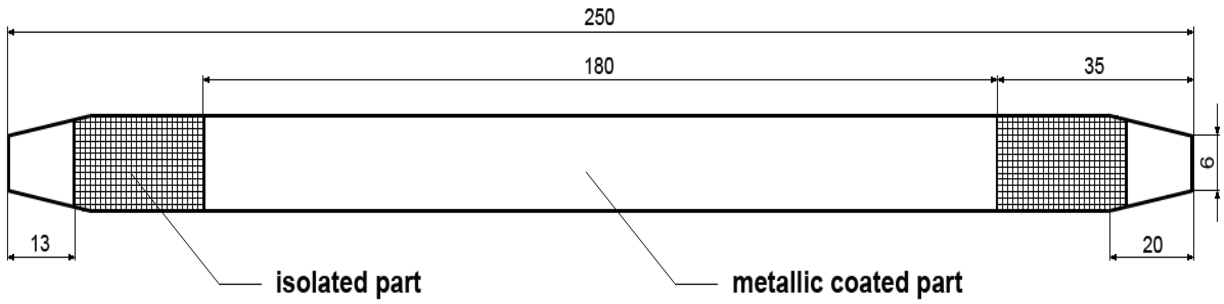

Figure 1. Shape and dimensions of the specimen used for determination of internal stresses

Table 1. Technological parameters of galvanic coating process

Electrolyte composition		Working conditions	
Component	Concentration [g.l^{-1}]	Parameter	Value
$NiSO_4 . 6H_2O$	640	pH	4
$CoSO_4 . 7H_2O$	20-45	Temperature	55 - 60 °C
$NiCl_2$	10-20	Current density	1 – 8 A.dm^{-2}
H_3BO_3	20-30		
Saccharine	1-2		

Macroscopic internal stresses of the coating system were measured with an IS meter, Fig 2. This instrument allows one to measure internal stresses in the course of galvanic coating.

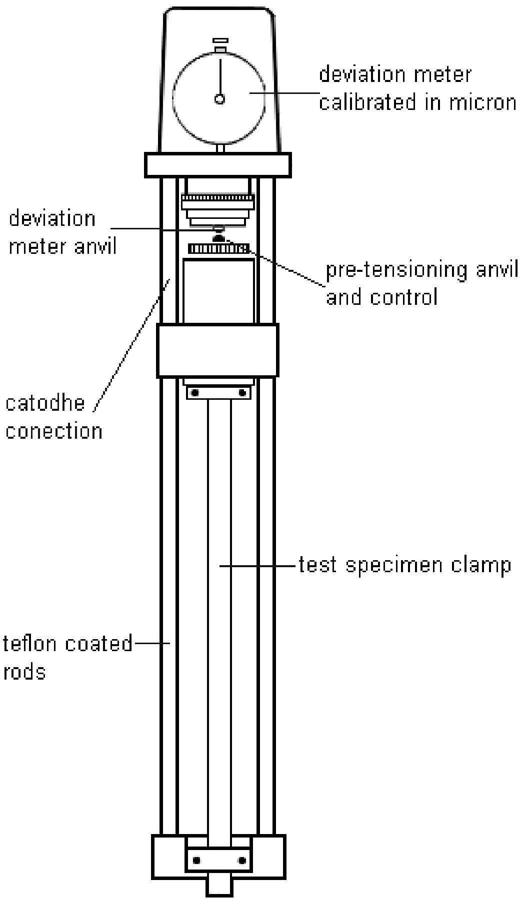

Figure 2. Scheme of the IS meter [3]

The measurement with IS meter is based on the measurement of elongation or shortening of specimens induced by internal stresses. The magnitude of compression or tensile stress is calculated according to the formula (1). When determining internal stress of the coated system, we used a calculation requiring dimensions of the specimen before and after coating. Using a micrometer, we measured the thickness of the steel band in three places. The specimen was clamped in the IS meter, degreased by preparation A.B.M, the part intended for coating was activated in an activation salt No. 5, or with preparation UNI Clean 698 for 10 seconds, and rinsed in demineralised water. By means of a holder the IS meter was immersed in a bath so that the specimen was covered with electrolyte. After the specimen warmed up to the required temperature and the linear changes on an indicator have stabilised, the indicator was set to zero and the specimen was connected to the current. The principle of determination of macroscopic internal stresses consisted in measurement by means of deviation meter of lengthening or shortening of the metal band that was galvanically coated on both sides, which induced internal stress in the specimen. Any linear changes were recorded in regular intervals for certain period. After termination of measurements and switching off the current, the specimen was rinsed with demineralised water, removed from the IS meter and the thickness of the deposited coating was measured with a micrometer in three places. The measurements made before and after coating served to determine the coating thickness. On the basis of comparison of individual measurements, we recalculated internal stresses in the measured specimens per 0.007 mm of the deposited coating (etalon). By means of calculation of the time $T_{0.007}$ we determined from the table of measured values the deformation of the specimen in μm.

The above determined deformation served to calculate the internal stress in the coating using the following formula:

$$\sigma = \left(E \cdot t_V / 2 \cdot 1 \cdot t_{0,007}\right) \cdot \Delta l \cdot 10^{-3} \quad (1)$$

where, σ – normal stress [MPa],
E- elasticity modulus of the material [MPa],
l – specimen length [mm],
$t_{0.007} = t_v + 0.007 + 0.007$ (coating deposited on two opposed surfaces),
Δl – lengthening (shortening) of the specimen [μm].

The same way of specimen preparation, measurement with IS meter and calculation of internal stresses was used for galvanic coating produced with addition of saccharin into the electrolyte.

3. RESULTS OF EXPERIMENTS AND DISCUSSION

Table 2. Values measured for the selected specimen, needed for calculation (1)

Parameter	Value
Thickness t_V [mm]	0.050
Thickness t_K [mm]	0.073
Length l [mm]	179
Modulus of elasticity E [MPa]	$1.95 \cdot 10^5$
Total time t_c [min]	34

The values measured according to the specified procedure were processed by means of the formula (1). We present calculation for selected specimen, providing in Table 2 the measured values needed for such calculation.

Using the values measured before and after coating, we determined the coating thickness as follows:

$$t_p = \frac{t_K - t_V}{2} \qquad (2)$$

where,

t_P – coating thickness [mm],
t_K – mean specimen thickness after coating [mm],
t_V – mean specimen thickness before coating [mm].

Considering the concrete values of Ni-Co specimen with Co concentration in the electrolyte 4 $g.l^{-1}$ and current density 3 Adm^{-2} (Fig. 4), the coating thickness is:

$$t_p = \left(\frac{0.064 - 0.051}{2}\right) = 0.006\ mm$$

The time needed for depositing of coating of thickness 0.007 mm was calculated according to formula:

$$T_{0.007} = \frac{T_C}{t_P} \cdot 0.007 \qquad (3)$$

where $T_{0.007}$ – is the time needed for depositing of coating of thickness 0.007 mm [min],
T_c – total coating time [min].
Considering the concrete values of the respective specimen:

$$T_{0.007} = \frac{15}{0.06} \cdot 0.007 = 15.7\ min.$$

On the basis of the measured values the total internal stress for the selected specimen calculated according to (1) was as follows:

$$\sigma = (1.95 \cdot 105 \cdot 0.051/2 \cdot 180 \cdot 0.065) \cdot 39 \cdot 10^{-3} = 16.8\ MPa$$ (shown in Fig. 4)

The same calculations were performed to determine internal stresses for all investigated specimens. Results of measurements of internal stresses in the Ni-Co coating in dependence on concentration of cobalt in the electrolyte at individual current densities are presented in Fig. 4.

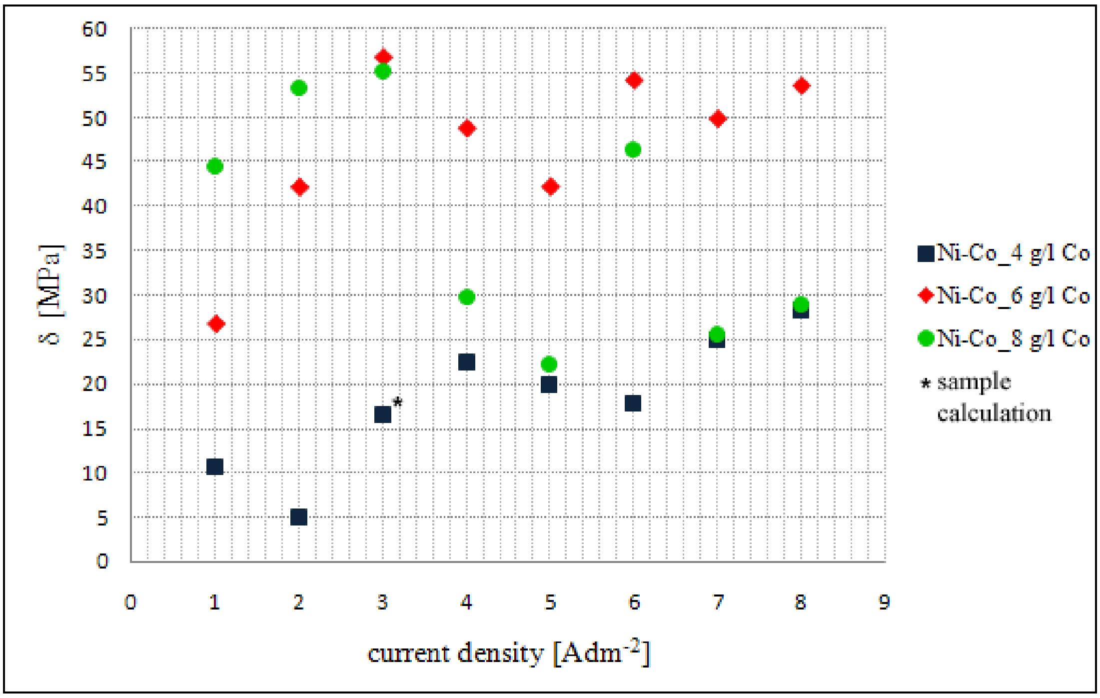

Figure 4. Magnitude of internal stresses in the Ni-Co coatings for individual concentrations of Co in the electrolyte in dependence on the current density

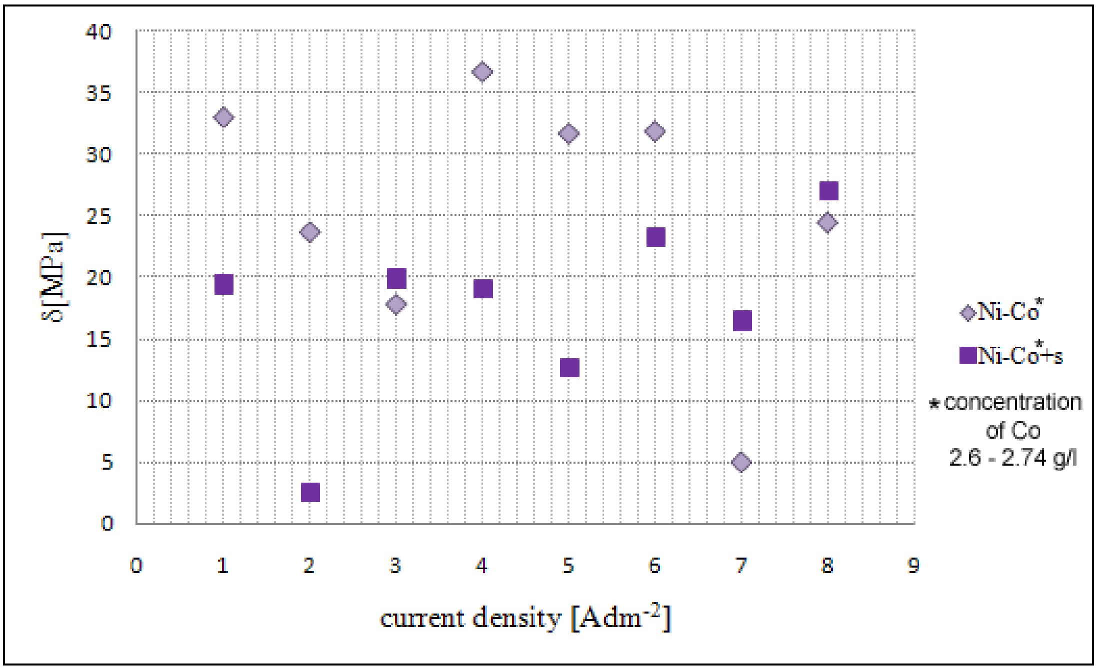

Figure 5. Internal stresses for Ni-Co coating without and with addition of saccharin into the electrolyte

The levels of internal stresses were determined and calculated also for specimens with deposited alloy Ni-Co coating without (Ni-Co) and with addition of saccharin (Ni-Co+s), Fig. 5.

Macroscopic internal stresses were determined by IS meter and calculated according to formulae (1) – (3). Magnitude of the internal stresses in Ni-Co coatings depends on current density during the coating process which is limited by concentration of cobalt in the electrolyte [3].

Fig. 4 shows the course of internal tensile stress δ in relation to current density for individual concentrations of cobalt in the electrolyte. This relationship shows an increasing tendency with the highest values at cobalt content of 6 g.l^{-1} and higher current densities of 6 Adm^{-2} and 8 Adm^{-2}. The lowest stresses δ, required also from the point of view of practical applications, were recorded at lowest cobalt concentration in the electrolyte of 2 g.l^{-1} and current density of 2 A.dm^{-2}. According to [15], very similar process conditions (1.75g.l^{-1} cobalt in the electrolyte and current density of 2 A.dm^{-2}) resulted in the highest levels of coating hardness of approx. 430 HV5.

Fig. 5 shows the magnitude of tensile stress in the Ni-Co coating without and with saccharin addition in relation to current density during the electrochemical process. Coating in the sulphamate electrolyte supplemented with saccharin resulted in lower level of internal stress in comparison with the coating deposited from electrolyte without an additive. Small concentrations of additive enhance nucleation, resulting in a chevron, high deposit ductility and low tensile strength [16]. For nickel and cobalt coatings are used grain refiners additives. According [15] the additive effect seen in an increase in the speed of nucleation sites. If the rate of nucleation is greater than the rate of growth of crystallites arising coating, resulting in a fine, closely disposed structure. Fine grained structure has (according Hall-Petch relation) a higher strength and hardness, too. A lower level stress provides a very good adhesion alloy coating and a good abrasion resistance. The lowest level of stress σ was measured in the electrolyte at current density of 2 A.dm^{-2} at concentration of cobalt in the electrolyte ranging between 2.6 and 2.74 g.l^{-1}.

4. CONCLUSION

The purpose of supplementing electrolyte with an additive is to reduce the unfavourable tensile stresses in the coatings. Management of the process technology allows one to obtain coatings with sufficiently good properties, adequate for their use.

Results of our experiments allowed us to state the following:

- The lowest concentration of cobalt in the electrolyte and the lowest current density, i.e. 4 g.l^{-1} and 2 A.dm^{-2}, resp., resulted in the lowest levels of the tensile component of internal stresses, namely 4.8 MPa,
- Addition of saccharine to the electrolyte at concentrations of cobalt 2.6 – 2.74 g.l^{-1} and the lowest current density of 2 A.dm^{-2} allowed us to measure the lowest levels of the tensile component of internal stresses, namely 2.56 MPa,
- The levels of internal stresses σ in the Ni-Co coatings, deposited from electrolytes with and additive were lower at the measured current densities in comparison with levels of δ in the coatings deposited in the electrolyte free from an additive.

Combination of parameters of electroplating process, particularly of current density and composition of electrolyte in the selected ranges allows one to change the levels of internal stresses in the deposited coatings. Their determination during the deposition process is important from the point of view of the electrochemical process the aim of which is a high quality coating.

ACKNOWLEDGEMENTS
The present results were obtained with the support of the Project VEGA 1/1123/12.

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