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The effect of a.c. superimposed on d.c. and pulsating potential on the coercivity of electrodeposited Ni–Fe alloy thin films

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The effect of d.c., a.c. superimposed on d.c. and constant and pulsating potentials on the coercivity of electrodeposited Ni–Fe alloy thin films obtained in a sulphate–tartrate bath has been investigated. It has been shown that the dependency of coercivity on current and potential parameters passes through a minimum. This phenomenon is related to the current efficiency of hydrogen production and to the alloy composition.

1. Introduction

The study of the electrodeposition and properties of Ni–Fe alloy thin films has become very important from both the theoretical and practical points of view. Electrodeposited alloys have applications in the electronic industries for magnetic shielding, memory devices for computers and recording tapes [1]. From a theoretical point of view, Ni–Fe alloy electrodeposition is very interesting, because it exhibits anomalous codeposition effects [2].

The methodology of the electrodeposition of thin magnetic films together with experimental results have been published in several papers [3–6]. In most cases the Ni–Fe films were electroplated from sulphate, chloride or sulphate–chloride baths. The magnetic properties of films produced in different baths show significant differences.

Coercivity is a very important magnetic property in the application range of feromagnetic materials. The desirable magnetic properties of films for memory units are a low coercive force and a square hysteresis loop. A coercive force indicates that the metal can be easily magnetized and demagnetized. According to Wolf [3], rectangularity of the hysteresis loop and coercivity of the Ni–Fe coatings depend very much on the deposit composition. The dependence of coercivity on the composition passes through a minimum, recognized for Ni–Fe alloys by a zero constant of magnetostriction. The differences in the coercivity dependencies on Ni–Fe alloy composition have been explained by the non-homogenous distribution of film stresses, caused by different substrate characteristics [7]. It was shown that the coercivity depends on the Ni–Fe alloy film thickness and is a function of the composition, substrate roughness, crystal size and structure and internal deposit stress.

The conventional way of electrodeposition of alloys is based on the use of d.c. Ni–Fe alloy thin films have been electrodeposited by periodically changing currents [8–11] and pulsating potential [12]. In these investigations it was shown that periodically changing currents and potentials affect the composition of electrodeposited Ni–Fe alloys appreciably. The variation of periodically changing current forms have considerable influence on the composition and magnetic properties of Ni–Fe alloy thin films [13].

The aim of this work was to investigate the effects of a.c. superimposed on d.c. and pulsating potential on the coercivity of Ni–Fe alloy thin films.

2. Experimental

The experiments were performed in a two-compartment cell. An electrolytic purity copper foil (thickness 0.1 mm and surface area 2.6 cm^2) was used as cathode; platinum foil was used as the counter electrode. The reference used was a saturated calomel electrode. Controlled d.c., a.c. super-imposed on d.c. and constant and pulsating potentials were applied to the system to be investigated by a potentiostat (PARC M173) driven by a function generator (PARC M175

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(for square-wave pulsating potential) or HP 3310 (for a.c.)). The shape of the signal input was controlled by an oscilloscope (Tektronix 5111A).

A bath containing 0.024 M $NiSO_4 \cdot 0.006\,M FeSO_4$ and 0.035 M $NaKC_4H_4O_6$ (pH = 4.6) was used to electrodeposit Ni-Fe alloy [9]. In d.c. conditions the Ni-Fe alloys were deposited in the current density range from 0.25 to 2.0 mA cm^{-2}. In the case of a.c. superimposed on d.c., the average current density of 1.0 mA cm^{-2} was used, while the ratio of amplitude of a.c. density (j_p) and d.c. density (j_{dc}) (at $\nu = 50$ Hz) or frequency (at $j_p/j_{dc} = 1.5$) were changed. In the potentiostatic plating conditions the nickel-iron alloys were deposited in the potential range from −900 to −1150 mV against SCE. In the case of the pulsating potential, the average potential value of −1020 mV against SCE (corresponding to the average current density of 1.0 mA cm^{-2}) was used, while the potential amplitude, E_p, (at $\nu = 100$ Hz) was varied in the range 25–300 mV. All experiments were carried out at room temperature (23 ± 1° C).

In order to avoid the thickness effect on the coercivity, the Ni-Fe alloys were deposited in a thickness range 300 ± 15 nm. The thickness was estimated from the total weight of the alloy deposited on a given area. After electroplating, the Ni-Fe alloy was dissolved in 1 : 4 HNO_3. The composition of the alloy was analysed spectrophotometrically. Current efficiency, *CE*, was calculated from the total weight of the nickel and iron in the alloy and the quantity of electricity passed during electrolysis. The coercivity of all samples was measured with a coercivimeter (Dr Foërster 1095).

3. Results and discussion

3.1. *Electrodeposition in d.c. conditions*

The dependence of the coercivity, H_c, of the thin Ni-Fe alloy films electrodeposited in d.c. conditions, on the current density is shown in Fig. 1. The coercivity, on the arbitrary scale presented, was obtained in such a way that the values for Ni-Fe alloy films were normalized to the coercivity value of a Ni-Fe alloy film produced in d.c. conditions at a current density of 1.0 mA cm^{-2}. It is seen that in the current density region from 0.25 to 2.0 mA cm^{-2}, the coercivity has a minimum at a current density of about 1.0 mA cm^{-2}. This type of coercivity dependence on the current density is in accord with the literature data [7, 13].

A very important factor affecting not only the composition, but also the Ni-Fe alloy properties, is the simultaneous hydrogen evolution during alloy deposition. Based on Dahms and Croll's theory [14], because of simultaneous hydrogen evolution during Ni-Fe alloy electrodeposition, the near cathode layer has an increased pH. Thus, $Fe(OH)_2$ and other hydrolysis products such as $Fe(OH)^{2+}$, $Fe(OH)^+$ etc., are produced on the cathode and incorporated into the deposit. The inclusion of the hydrolysis products in the deposit causes a deleterious effect on the magnetic properties of the plated Ni-Fe alloy [6].

An increase in current density from 0.25 to 0.1 mA cm^{-2} leads to a decrease in the current efficiency of hydrogen. This is clearly shown in Fig. 1. Based on this, and according to Dahms and Croll's theory, the tendency of the Fe^{2+} ion to form $Fe(OH)_2$, which is adsorbed on the cathode surface and incor-

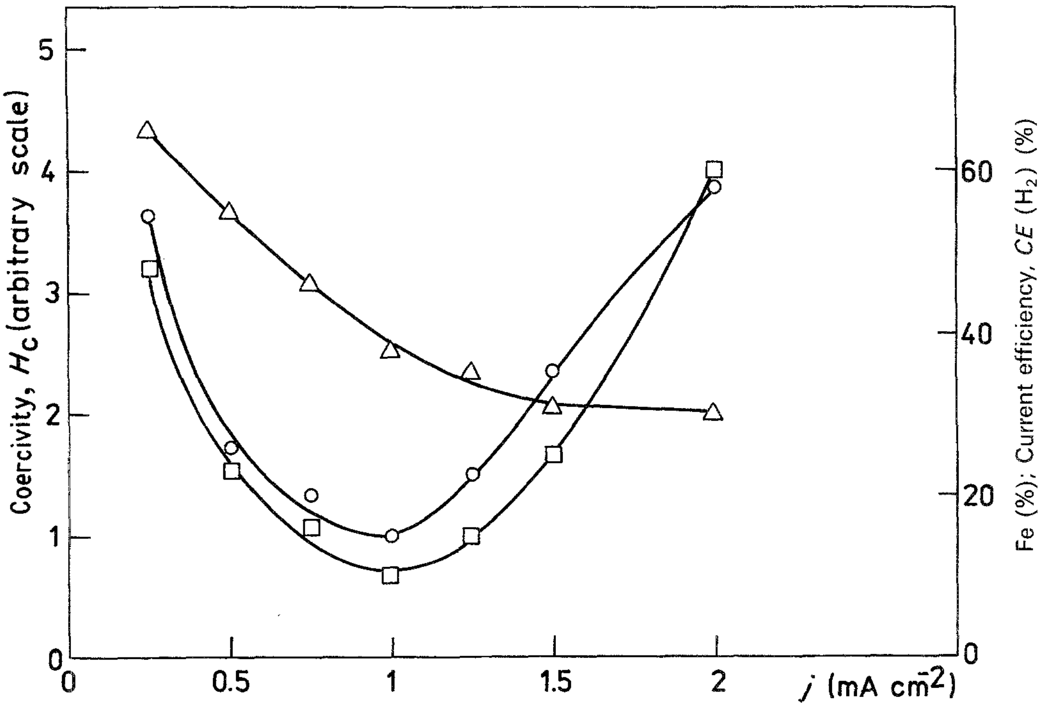

Fig. 1. The effect of d.c. density on the coercivity, $CE(H_2)$ and %Fe: △, %Fe; ○, H_c; □ $CE(H_2)$.

porated into the alloy deposit, decreases as the current density increases up to 1 mA cm^{-2}. Thus the coercivity decreased and approaches a minimum if the current efficiency of hydrogen has a minimum and the efficiency of Ni–Fe alloy has a maximum. If current density increases above 1 mA cm^{-2} the current efficiency of hydrogen also increases (Fig. 1). In this condition there is a high probability of $Fe(OH)_2$ formation and incorporation into the deposit, causing the coercivity to increase.

3.2. *The effect of a.c. superimposed on d.c. on the coercivity of Ni–Fe alloys*

In the work with a.c. superimposed on d.c., the influence of the current density amplitude and a.c. frequency on the coercivity of thin Ni–Fe films has been investigated. Although high variation in Ni–Fe alloy composition, influenced by change of a.c. parameters, was not observed [11], the experiments are based on the fact that this current type obtained is practically very simple. On the other hand, in the literature relative to electrodeposition of Ni–Fe alloys by periodically changing current, most studies have concentrated on use of a.c. superimposed on d.c. [13].

Figure 2 shows the dependence of coercivity on the j_p/j_{dc} ratio. With increase of the j_p/j_{dc} ratio in the range 0–1.5, the coercivity shows a slow decrease. With further increase of this current ratio the coercivity also increases.

The periodically changing current parameters affect the Ni–Fe alloy composition only when the Q_c/Q ratio is higher than 1 (where Q_c is the cathodic quantum of electricity and Q is total quantum of electricity), which in the case of a.c. superimposed on d.c. is realized only for $j_p/j_{dc} > 1$ [11]. Thus with change of the j_p/j_{dc} ratio within the interval 0–1.5, the coercivity decreases slowly.

As shown, during electrodeposition of Ni–Fe alloys by periodically changing current, the current efficiency of nickel deposition is practically constant [11]. With a.c. amplitude increase, the iron content in the alloy and the current efficiency of iron decrease, but the current efficiency of hydrogen production increases, as shown in Fig. 2. In such conditions the probability of $Fe(OH)_2$ formation and its inclusion into the deposit increases and coercivity increases for $j_p/j_{dc} > 1.5$.

Frequency dependence of the coercivity is shown in Fig. 3. Obviously, this dependence has a minimum at a frequency of about 50 Hz. With frequency decrease (< 50 Hz) a non-stationary phenomenon of periodically changing current becomes obvious. In this case the Fe content in the alloy is decreased, whereas the current efficiency of hydrogen production is increased (Fig. 3). Therefore the coercivity of Ni–Fe alloy films is increased.

With frequency increase a damped Faradaic current appears and in such a case the behaviour characteristic of d.c. itself is dominant [15]. Thus coatings obtained at frequencies above 100 Hz have almost the same quality as those obtained by electrolysis carried out in d.c. conditions at current density of 1.0 mA cm^{-2}. Therefore, the coercivity of the Ni–Fe alloy films in the frequency range over 100 Hz is practically constant.

3.3. *The effect of constant potential on the coercivity of Ni–Fe alloy*

The dependence of coercivity on the plating potential

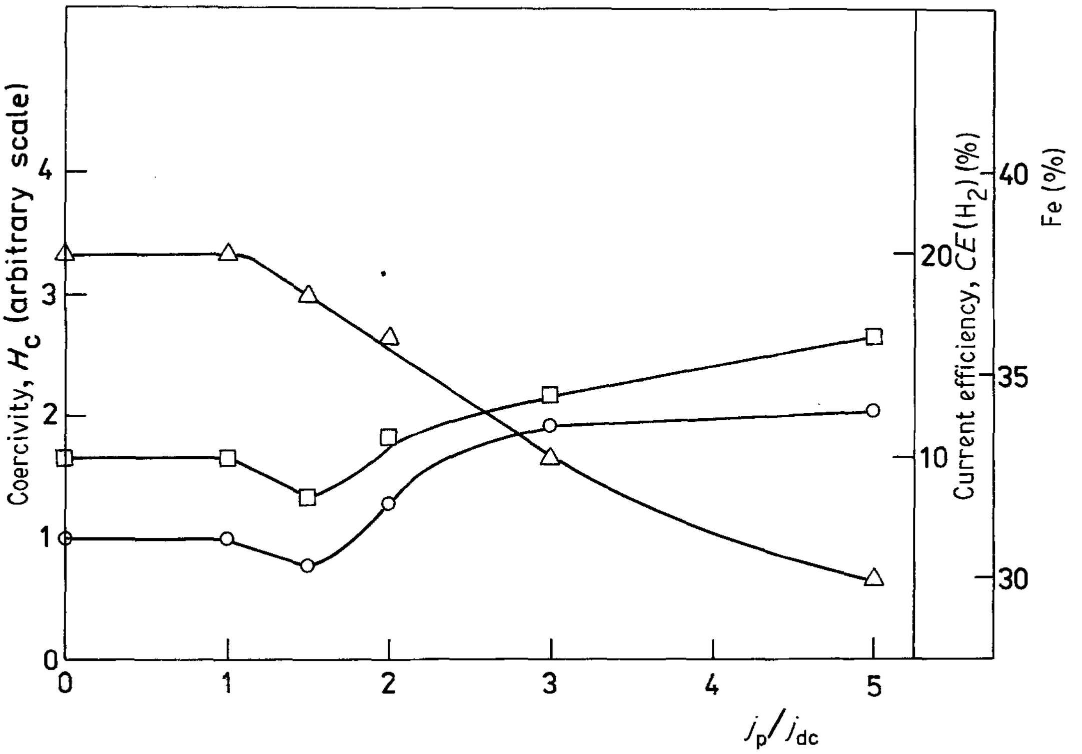

Fig. 2. The effect of the j_p/j_{dc} ratio on the coercivity, $CE(H_2)$ and %Fe (j_{dc} = 1.0 mA cm^{-2}, ν = 50 Hz): △, %Fe; ○, H_c; □, $CE(H_2)$.

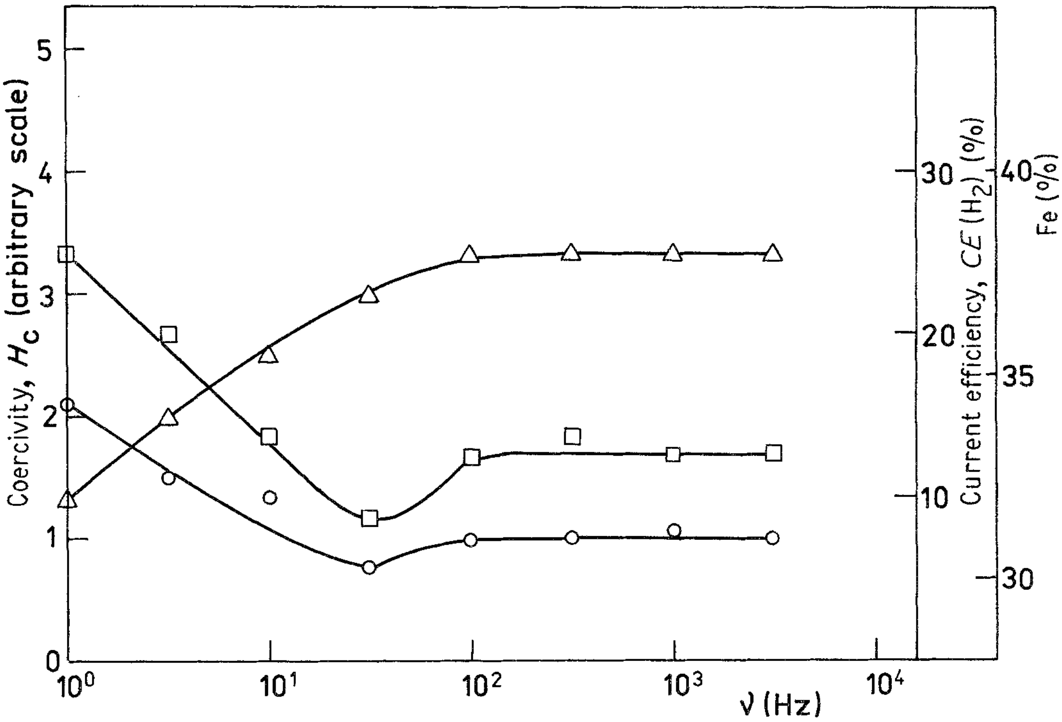

Fig. 3. The effect of a.c. frequency on the coercivity, $CE(H_2)$ and %Fe ($j_p/j_{dc} = 1.5$): △, %Fe; ○, H_c; □, $CE(H_2)$.

is shown in Fig. 4. Within the range −950 to −1100 mV the coercivity shows a minimum at a potential of −1020 mV (corresponding to the average current density of 1.0 mA cm^{-2} [12]). From Fig. 4 it can also be seen that, within the potential range −950 to −1020 mV, the current efficiency of hydrogen production decreases. With further negative increase of the potential (within the range −950 to 1020 mV), as well as in galvanostatic plating conditions, the coercivity decreases with decrease of Fe content in the Ni-Fe alloys and the current efficiency of hydrogen production. However, the further increase in the potential (above −1 075 mV) causes poor quality of the coating owing to intense hydrogen evolution and exceeding of the limiting current density [12]. Thus with a potential increase above −1020 mV, the quantity of hydrolysis products adsorbed and incorporated into the deposit of the Ni-Fe alloy is increased, which caused the coercivity to increase.

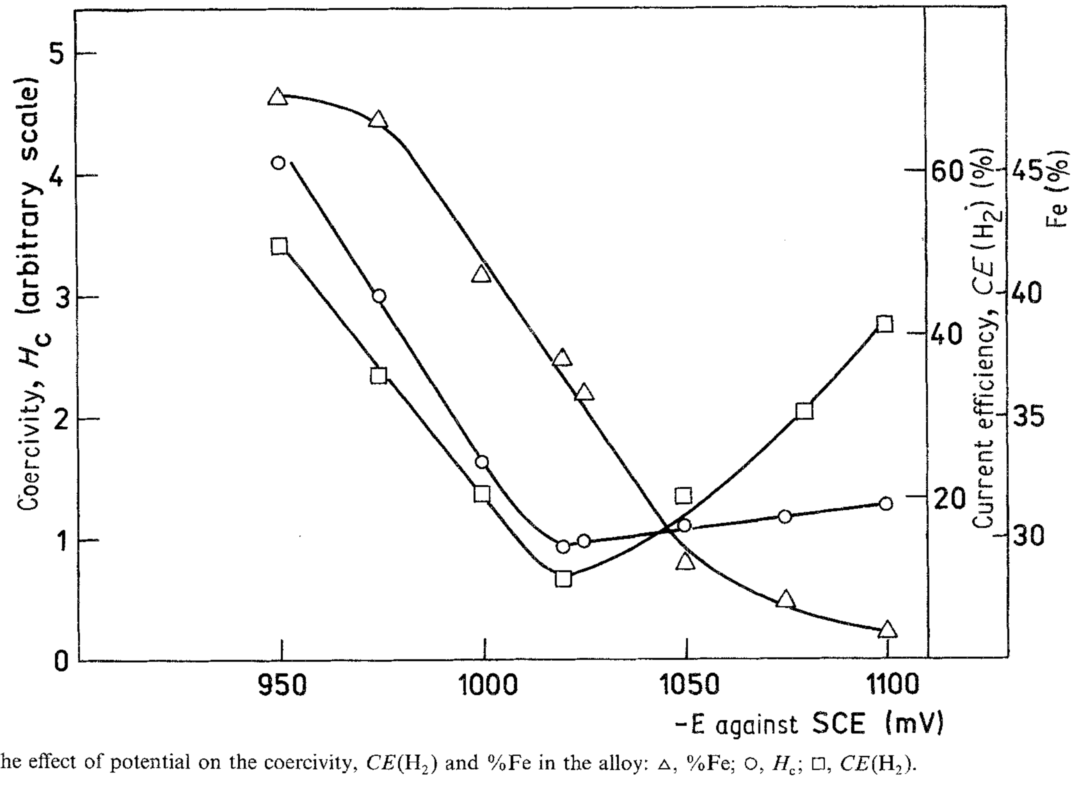

Fig. 4. The effect of potential on the coercivity, $CE(H_2)$ and %Fe in the alloy: △, %Fe; ○, H_c; □, $CE(H_2)$.

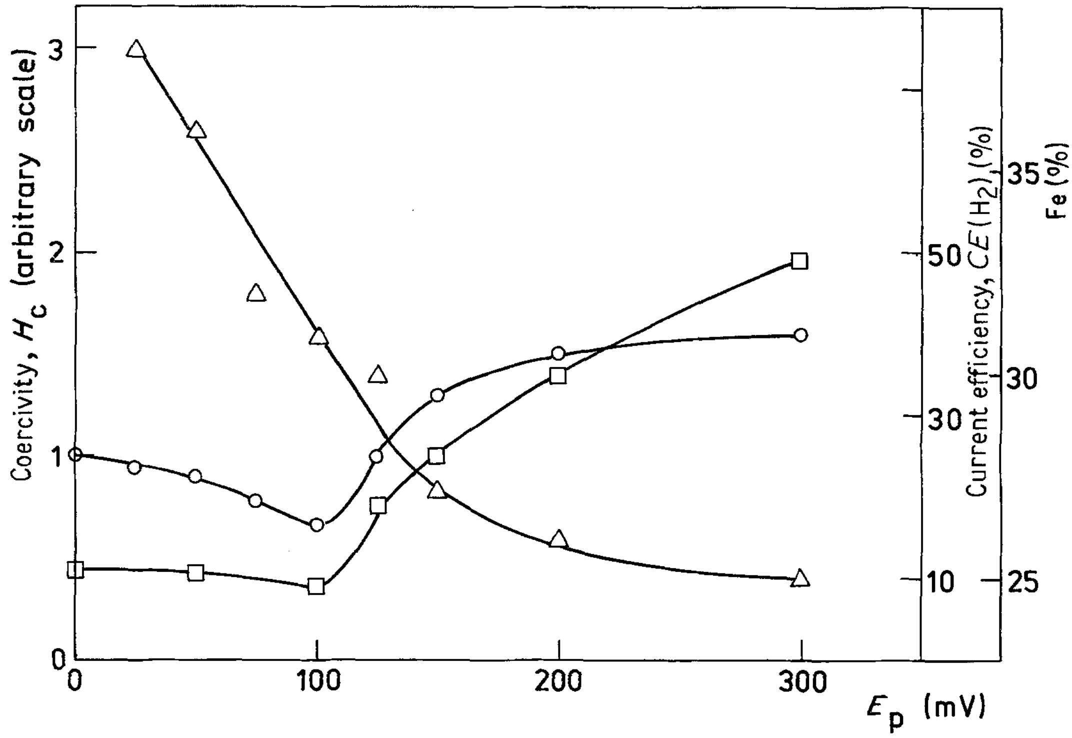

Fig. 5. The effect of pulsating potential amplitude on the coercivity, $CE(H_2)$ and %Fe in the alloy (E_{av} = 1020 mV, ν = 100 Hz): △, %Fe; ○, H_c; □, $CE(H_2)$.

3.4. *The effect of pulsating potential on the coercivity of Ni–Fe alloy*

In the case of pulsating potential, the effect of potential amplitude on the coercivity has been investigated. These experiments were performed because the relatively small variation of pulsating potential amplitude leads to considerable change of alloy composition [12]. The results presented in Fig. 5 show that with a potential amplitude increase up to 100 mV, the coercivity decreases. For the potential amplitude of 100 mV, a minimum coercivity is reached. With further pulsating potential amplitude increase (from 100 to 200 mV), the coercivity increases. With pulsating potential amplitude above 200 mV, the coercivity of the Ni–Fe alloy does not vary significantly and coatings with black edges are produced.

When the pulsating potential amplitude increases to 100 mV, the Fe content in the alloy and the coercivity decrease. With further decrease of pulsating potential amplitude, the Fe content in the alloy also decreases, but the coercivity increases. The experiments with pulsating potential show that the alloy composition is mostly influenced by the most negative potential [12]. Similarly, the most negative value of potential probably shows the strongest effect on coercivity. With increase of potential amplitude (above 100 mV), the current efficiency of hydrogen production increases (Fig. 5). In these conditions, the quantity of hydrolysis products absorbed and incorporated into the Ni–Fe alloy is increased thus causing a low quality of coating and the associated coercivity increase.

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