

Electropolishing of AISI-304 stainless steel using an oxidizing solution originally used for electrochemical coloration

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Abstract

Chemical polishing or electropolishing, instead of mechanical polishing, are recommended for the attainment of metallic surface polishes without the introduction of contaminants or tensions in the surface layers of the metal. The fundamental difference between the chemical and electrochemical polishing processes is that in the latter anodic currents/potentials are used to help in the dissolution and passivation of the metal. In this paper, the use of an oxidizing electrolytic solution ($2.5 \text{ mol L}^{-1} \text{ CrO}_3 + 5.0 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$) originally employed in electrochemical coloration processes is reported for the electropolishing of AISI-314 stainless steel. Parameters involved in this electropolishing process, such as temperature, current density and time, were optimized so as to attain the best possible results evaluated by the obtained surface brightness measured by reflectance spectra. Surface analyses by scanning electron microscopy allowed a clear correlation between obtained brightness and surface smoothing. The best conditions obtained for the electropolishing process are: temperature of 45°C , electrolysis time of 10 min and current density of around 25 A dm^{-2} . It should be pointed out that an electropolishing process signature (periodic oscillations of the cell potential) was established; this may be an important tool for optimizing and monitoring electropolishing processes.

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1. Introduction

In spite of the numerous applications of stainless steels (from silverware to reactors in the chemical industry), their standard color – light gray – does not always harmoniously fit in the environment where they are used. Thus, adequate surface treatments of stainless steels, specially their coloration, can lead to more diversified uses of them. This coloration can be obtained by different methods: chemical oxidation [1], thermal oxidation [2], and electrochemical oxidation [3–8]. However, it is well known that the quality of the coloration of stainless steel is strongly dependent on the initial state of the metal surface; hence, previously to submitting the steel

to the coloration process, it is necessary to polish its surface. For this end the choice of the polishing method depends not only on the type of finishing desired but also on the state of the metal surface.

Mechanical polish or grind is a good polishing method, but it has the disadvantage of hardening the surface, inducing a degree of residual tension and oxide incorporation, introducing scratch marks and damaged layers [9]. On the other hand, chemical polishing does not induce surface tensions and removes the surface by chemical dissolution, promoting the preferential removal of surface roughness, but at relatively slow rates. In electrochemical polishing, or electropolishing, the dissolution rate of the metallic surface is significantly increased by the application of anodic currents [10,11].

Electropolishing, generally defined as the improvement of the surface finish of a metal effected by making it anodic in an appropriate solution, can be used for different purposes:

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(i) removal of deformations in metallic surfaces, e.g., non-metallic inclusions, being an important tool in the fabrication of nuclear equipment, high-pressure vessels and fan blades for jet engines; (ii) electropolish of reactors, tubes, installations, valves, heat exchangers, making these materials more corrosion resistant and with a smooth, easily cleaned surface, and (iii) removal of burrs from metallic machines after blanking or milling processes, sharpening of tools, control of the dimensions of measurement instruments, smoothing of machine parts subjected to friction [10–13].

In electropolishing, in which the solutions used are commonly acidic, anodic currents or potentials lead to dissolution and passivation of the metal, promoting the leveling of the metal surface. In comparison with chemical polishing, these anodic conditions allow the use of less concentrated acid solutions, the achievement of better control and less duration of the process [11,14–17]. The electrochemical characteristics of electropolishing are such that the metal cannot passivate but also cannot undergo accelerated dissolution [11,14,17]. As a rule, the solutions used in the electropolishing of stainless steel contain strong acids (sulfuric, sulfuric/phosphoric/chromic, perchloric in methanol) [11,14,18]. On the other hand, the characteristics of a polished surface are such that it needs to be leveled at the macroscopic level (macrosmoothing or anodic leveling) and smooth and bright at the microscopic level (from 1 to 100 nm) for metals of very small grains (microsmoothing or anodic brightening) [14]. To attain these characteristics, the solutions used in the electropolishing must comply to three requisites [11], so that:

- they must be capable of dissolving metal in solution through a surface film which smoothes any preferential dissolution on an atomic level;
- they should provide for control of the oxide film thickness—if too thick the metal passivates and polishes extremely slowly, if too thin or absent preferential etching can occur;
- they should favor the formation of a viscous diffusion layer promoting macroscopic leveling.

The characterization of an electropolishing process is carried out through its polarization curve (current density versus potential) [11,14], obtained under stationary state conditions. Processes that work adequately are associated to a wide potential range at constant current (polishing plateau), but the value of that constant current can be fairly critical [11,12,14]—if it is too small the metal is passivated, if excessively large the metal dissolves under solution diffusion control but heating may cause surface deterioration, in neither case leading to effective electropolishing.

A strongly oxidizing solution (5.0 mol/L H_2SO_4 + 2.5 mol/L CrO_3), similar to the ones used in electropolishing processes [10], has been used in our laboratory in studies of electrolytic coloration processes of stainless steel at room temperature [7,8]. In one of those coloration experiments, by accident it was observed that the stainless steel samples besides being colored could also be electropolished in that

solution; from a technological point of view, this fact leads to a highly desirable situation. Thus, taking into account the several works reported in the literature on the electropolishing of stainless steels [9,10,18–22] and the promising possibility of using a same solution for their electropolishing and coloration, the present paper deals with the development of this $\text{H}_2\text{SO}_4/\text{CrO}_3$ electropolishing bath for AISI-304 stainless steel. The influences of temperature, applied current and time were investigated; the obtained results were followed by reflectance and scanning electron microscopy measurements.

2. Experimental

2.1. Sample preparation

Specimens of AISI-304 stainless steel (Acesita # 2B) of size 5.0 cm × 1.0 cm × 0.1 cm were cut and their sides were ground to remove burrs. They were degreased with acetone, under ultrasonic vibrations, for 10 min at room temperature. Previously to electropolishing the specimens were cathodically polarized (0.1 A dm^{-2}) in $1.0 \text{ mol L}^{-1} \text{ HNO}_3$ for 15 min. Then, after weighing, they were immersed in aqueous $5.0 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4 + 2.5 \text{ mol L}^{-1} \text{ CrO}_3$, at different temperatures ($30^\circ\text{C} \leq \theta \leq 55^\circ\text{C}$), and anodically polarized ($20 \text{ A dm}^{-2} \leq i \leq 40 \text{ A dm}^{-2}$) for different times (up to 30 min); afterwards, the specimens were weighed again. A TCA/Tectrol 30 V–5 A power supply was used to control the applied current and the bath temperature was controlled using a thermostat.

2.2. Characterizations

The electropolishing process was electrochemically characterized through the use of chronopotentiometry, using a one-compartment cell. Two graphite plates ($\sim 10 \text{ cm}^2$) were used as counter electrodes; no reference electrode was used.

The evaluation by visual inspection of the quality of the surface polish was checked by spectral reflectance measurements carried out in a model 17 Cary spectrometer. The wavelength was scanned from 400 to 800 nm at a scanning rate of 5.0 nm/s. Analyses of the state of the surface of the stainless steel specimens were carried out by scanning electron microscopy (SEM) at magnifications of $1000\times$.

3. Results and discussion

Initially the effect of temperature (30, 35, 40, 45, 50 and 55°C) on the quality of the surface polish was investigated. For such, at each temperature the current density was set at $\sim 30 \text{ A dm}^{-2}$ and the electropolishing time was varied: 5, 10, 15, 20, 25 and 30 min. Fig. 1 shows the values of mass loss for each sample as a function of the bath temperature, for the different electropolishing times. For electropolishing times less than 25 min there is a tendency for the mass loss

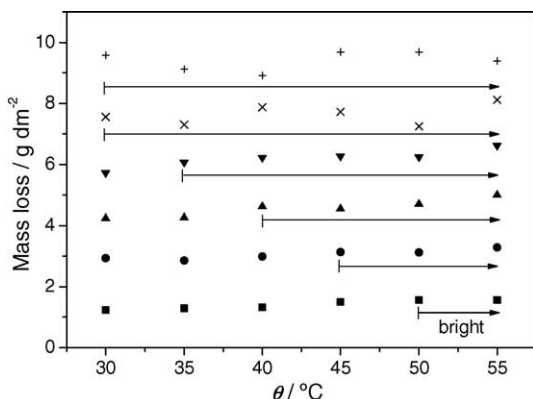


Fig. 1. Electrolyzed sample mass loss vs. electrolyte temperature, for different electrolysis times at 30 A dm^{-2} : (■) 5 min, (●) 10 min, (▲) 15 min, (▼) 20 min, (×) 25 min and (+) 30 min. The arrows indicate the temperature range at which bright electropolishes were obtained for each electrolysis time.

to slightly increase with the bath temperature, up to around 15%; on the other hand, for the times 25 and 30 min the mass loss values simply oscillate around a constant value. This irreproducibility in the mass loss for the longer times may be due to bath temperature variations as a consequence of Joule heating. On the other hand, it should be pointed out that the time necessary to obtain a bright polished steel surface decreased with the bath temperature, as indicated by the arrows in Fig. 1. For example, at 30°C , brightness was obtained after electropolishing times ≥ 25 min, while at 50°C it was obtained after only 5 min. From this figure one can infer that the mass loss increases by about the same value for each 5-min increase in the electropolishing time. For the bath temperature of 45°C , a linear relationship between mass loss and electropolishing time is observed, corresponding to a rate of mass loss of $0.32 \text{ g dm}^{-2} \text{ min}^{-1}$; in another words, the mass loss after each 5 min of electropolishing is slightly greater than 1.6 g dm^{-2} .

Fig. 2 shows the strong influence of the temperature on the chronopotentiometric profiles obtained for electrolysis carried out at 30 A dm^{-2} , for 10 min. When the electrolysis is carried out at 30°C , a response typical of passivation is obtained, with the cell potential stabilizing around 3 V after

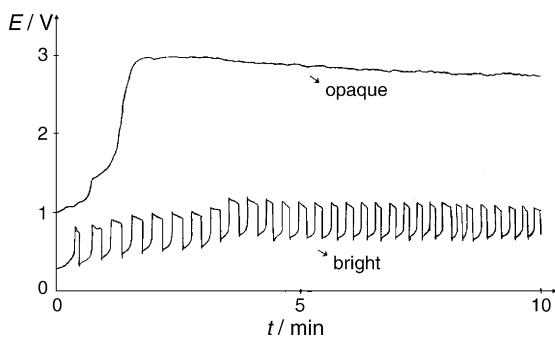


Fig. 2. Cell potential vs. electrolysis time for an electropolishing process that yields an opaque sample surface (30 A dm^{-2} , 30°C and 10 min) and for one that yields a bright sample surface (30 A dm^{-2} , 45°C and 10 min).

about 2 min; hence, the sample is not electropolished and consequently no brightness is observed. On the other hand, when the electrolysis is carried out at 45°C , an oscillating potential response is obtained, associated to the occurrence of surface film formation (reflected in the potential increase), surface passivation (reflected in the potential stability) and film dissolution (reflected in the potential decrease). In fact, this potential oscillation behavior has been found to be a typical signature of effective electropolishing processes.

Once this signature was clearly established, chronopotentiometric profiles (Fig. 3) were obtained for samples electrolyzed at 50 and 55°C . They clearly indicate that the frequency of occurrence of surface passivation and film dissolution is increased with the temperature. Hence, it can be concluded that higher temperatures facilitate the AISI-304 stainless steel electropolishing process. Landolt and coworkers [23,24] showed that there is a change of mechanism with the temperature, from a kinetic to a diffusion-controlled process, which leads to polishing conditions.

Nevertheless, the choice of the best conditions to carry out the electropolishing process must be such that energy consumption is minimized, i.e. shortest possible electrolysis times at an adequate solution temperature (the lowest temperature at which the typical chronopotentiometric signature is present). Thus, with the goal of optimizing the quality of the electropolish as a function of the current density in experiments carried out at 45°C , the electropolishing time was varied at different current densities. The obtained results allowed the conclusion that the stainless steel dissolution rate ($DR = m/t$) increases linearly with the current density, as shown in Fig. 4. Furthermore, by following the quality of the obtained electropolished surfaces, a range of current density (and coupled range of DR) at which the surface brightness is satisfactory could be defined: $25\text{--}35 \text{ A dm}^{-2}$ (or $7.0\text{--}9.5 \text{ mg min}^{-1}$). Considering that the quality of the electropolished surface obtained in these conditions is

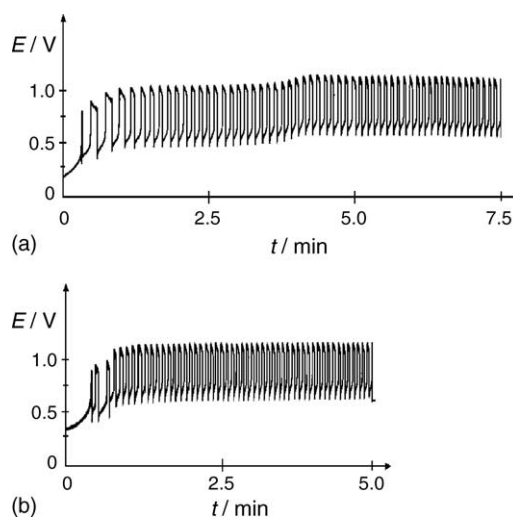


Fig. 3. Cell potential vs. electrolysis time for electropolishing processes (30 A dm^{-2}) at 50°C (a) and 55°C (b).

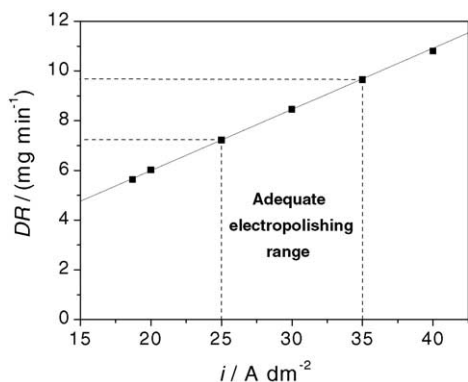


Fig. 4. Sample dissolution rate ($DR = m/t$) vs. current density, at 45 °C.

the same, the optimum parameters for the galvanostatic electropolishing process of AISI-304 stainless steel in the aqueous $5.0 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4 + 2.5 \text{ mol L}^{-1} \text{ CrO}_3$ electrolyte could be defined as 25 A dm^{-2} , 45 °C and 10 min. In principle, the slope of the line shown in Fig. 4 could be used to evaluate the apparent valence of metal dissolution [23]; if this is done, a value of 4.4 is obtained. However, considering that the major alloying elements of stainless steel are dissolved as Ni^{2+} , Fe^{3+} and Cr^{6+} , and that Ni is being dissolved in the same proportion as that in the metal (7.4%), the value 4.4 for the apparent valence of metal dissolution would be obtained only if about 48% of the species being dissolved were chromium. This is not reasonable at all; clearly the above procedure is not suitable for the evaluation of the apparent

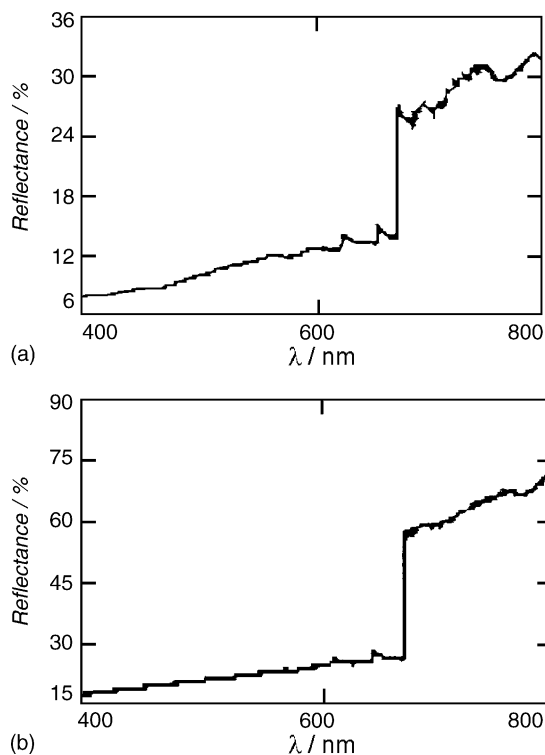


Fig. 5. Reflectance spectra for electropolished samples whose surface were classified as semi-bright (a) and bright (b).

valence of metal dissolution, because during galvanostatic electropolishing significant oxygen evolution is also present.

As soon as each electropolished surface was obtained, its polish quality was evaluated by visual inspection and classified in one of the following categories: bright, opaque or semi-bright. A reflectance measurement (Fig. 5a) obtained for a sample classified as semi-bright presented a maximum reflectance value of about 33%, when compared to that of an aluminum mirror. On the other hand, for a sample classified as bright, the maximum reflectance was of about 75% (see Fig. 5b). It should be noted that the step in the reflectance values that occurs around 700 nm in both spectra is due to a change of detector during the wavelength scan.

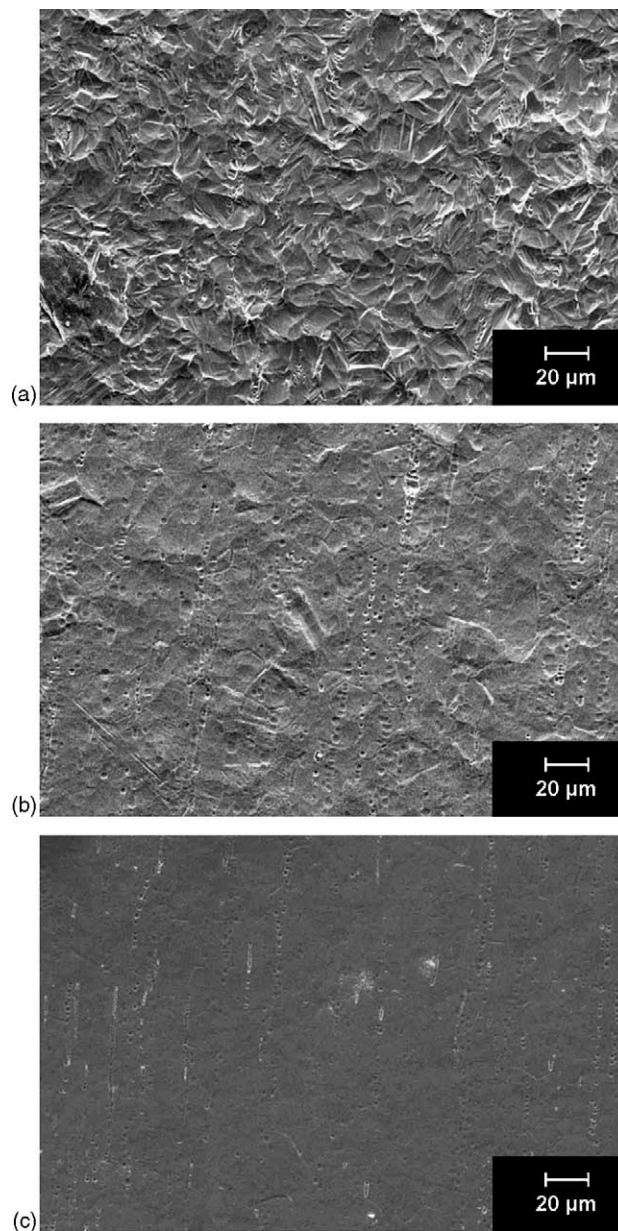


Fig. 6. SEM micrographs of electropolished samples whose surface were classified as opaque (a), semi-bright (b) and bright (c).

Jeyashree et al. [19] mentioned values of reflectance in the range 90–100% using a phosphoric/sulfuric electropolishing solution ($7.4 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4 + 6.5 \text{ mol L}^{-1} + 0.33 \text{ mol L}^{-1}$ ethanolamine) at 31 A dm^{-2} for near 10 min; however the temperature used was in the range 60–80 °C.

The analysis of the surface of the electropolished samples by SEM—scanning electron microscopy (Fig. 6) allowed the characterization of the surface states obtained under different electrolysis conditions that lead to different brightness intensities. The SEM micrograph obtained for a steel sample electrolyzed under conditions that led to a surface classified as opaque (Fig. 6a) reveals a quite rugose surface. The SEM micrograph obtained for an electrolyzed steel sample classified as semi-bright (Fig. 6b) shows that, as it was expected, the surface roughness was significantly decreased, compared to that shown in Fig. 6a. Additionally, the SEM micrograph obtained for an electropolished steel sample classified as bright (Fig. 6c) shows that the steel surface became quite uniform and leveled, practically without any roughness whatsoever. These results clearly confirm, as it was expected, that the steel surface brightness intensity is directly related to the state of the obtained electropolished surface.

Finally, considering that the quality of an obtained electropolish might depend on the total time of electrolytic-solution usage (due to diminishing acidity), this was also investigated, by carrying out repetitive electrolyses for 10 min at the optimal experimental conditions (see Fig. 4) until the quality of the electropolish became deteriorated. The results thus obtained indicated that electropolishes of good quality can be obtained up to a maximum value of $\sim 100 \text{ kC L}^{-1}$ for the ratio electrolysis charge/electrolyte volume.

4. Conclusions

The quality of the surface obtained by an electropolishing process strongly depends on the electrolyte properties [11]. Thus it becomes essential to know which factors affect the electropolishing qualities of the electrolyte here reported ($5.0 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4 + 2.5 \text{ mol L}^{-1} \text{ CrO}_3$), in order to have a good control of the process and to minimize unexpected results. Furthermore, the optimizing of an electropolishing process requires the achievement of total control of the involved variables (temperature, electrolysis time, current density, mass loss) so as to be sure that it will lead to an adequately bright surface.

For the new electropolishing electrolyte here presented, the search for the shortest possible electropolishing time was successful by increasing the electrolyte temperature, obtaining a minimum time of 5 min but for a temperature of 55 °C. However, these conditions were not considered desirable due to the higher temperature used. Hence, the best conditions obtained for the electropolishing process were considered to be the following: temperature of 45 °C, electrolysis time of 10 min and current density of around 25 A dm^{-2} . The qual-

ity of the electropolishes, preliminarily assessed by visual inspection, could be confirmed by reflectance spectroscopy measurements as well as scanning electron microscopy. The possibility of using a same solution for the electropolishing and coloration of AISI-314 stainless steel is a quite welcome outcome. Of course, appropriate care has to be taken when using this solution due to environmental and health hazards.

Finally, it should be pointed out that a clear correlation between periodic oscillations of the cell potential and electropolishing occurrence could be established. This electropolishing signature may be an important tool for optimizing and monitoring electropolishing processes.

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References

- [1] T.E. Evans, A.C. Hart, A.E. Skedgell, *Trans. Inst. Met. Finish.* 51 (1973) 108.
- [2] S.A. Sygeoda, Belgium Patent 869,885 (February 1979).
- [3] K.M. Ogura, M. Tsujigo, K. Sakurai, J. Yano, *J. Electrochem. Soc.* 140 (1993) 1311.
- [4] S. Fujimoto, T. Shibata, K. Wada, T. Tsutae, *Corros. Sci.* 35 (1993) 147.
- [5] C.J. Lin, J.G. Duh, *Surf. Coat. Technol.* 85 (1996) 175.
- [6] K. Ogura, W. Lou, M. Nakayama, *Electrochim. Acta* 41 (1996) 18.
- [7] R. Conrado, N. Bocchi, R.C. Rocha-Filho, S.R. Biaggio, *Electrochim. Acta* 48 (2003) 2417.
- [8] E. Kikuti, R. Conrado, N. Bocchi, S.R. Biaggio, R.C. Rocha-Filho, *J. Brazil. Chem. Soc.* 15 (2004) 472.
- [9] E.S. Lee, *J. Adv. Manuf. Technol.* 16 (2000) 591.
- [10] W.J.MeG. Tegart, *The Electrolytic and Chemical Polishing of Metals*, 2nd ed., Pergamon Press, London, 1959.
- [11] D.R. Gabe, in: L.L. Sheir, R.A. Jarman, G.T. Burstein (Eds.), *Corrosion*, vol. 2, Butterworths-Heinemann, Oxford, 1994, pp. 11:24–11:39.
- [12] N.P. Fedot'ev, S.Ya. Grilikhes, *Electropolishing, Anodizing and Electrolytic Pickling of Metals*, Robert Draper, Teddington, 1959.
- [13] L.J. Durney, *Electroplating Engineering Handbook*, 4th ed., Van Nostrand-Reinhold, New York, 1986.
- [14] D. Landolt, *Electrochim. Acta* 32 (1987) 1.
- [15] R. Vidal, A.C. West, *J. Electrochem. Soc.* 142 (1995) 3389.
- [16] O. Piotrowski, C. Madore, D. Landolt, *Electrochim. Acta* 44 (1999) 3389.
- [17] C.L. Faust, *Met. Finish.* 82 (1984) 29.
- [18] S. Mohan, D. Kanagaraj, R. Sindhuja, S. Vijayalakshmi, N.G. Renganathan, *Trans. Inst. Met. Finish.* 79 (2001) 140.
- [19] G. Jeyashree, A. Subramanian, T. Vasudevan, S. Mohan, R. Venkatachalam, *Bull. Electrochem.* 16 (2000) 388.
- [20] T.S. Hahn, A.R. Marder, *Metallography* 21 (1988) 365.
- [21] V. Vignal, J.C. Roux, S. Flandrois, A. Fevrier, *Corros. Sci.* 42 (2000) 1041.
- [22] S.G.S. Raman, K.A. Padmanabhan, *Int. J. Fatigue* 17 (1995) 179.
- [23] M. Matlosz, D. Landolt, *J. Electrochem. Soc.* 136 (1989) 919.
- [24] M. Matlosz, S. Magaino, D. Landolt, *J. Electrochem. Soc.* 141 (1994) 410.