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Evaluation of the mechanical properties and corrosion behaviour of ultra-clean steels

R. Mendoza[a], M. Alanis[a], J. Huante[a], C. Gonzalez-Rivera[b], J.A. Juarez-Islas[b,*]

[a]*Ispat Mexicana S.A. de C.V., Fco. J. Mujica No 1B, Cd. Lazaro Cardenas Michoacan, Mexico*
[b]*Instituto de Investigaciones en Materiales — UNAM, Circuito Exterior S/N,*
Cd. Universitaria, O4510 Mexico, Mexico

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Abstract

Three ultra-low carbon/titanium (Ti) added steels in the as-annealed condition were evaluated in order to determine their mechanical properties, in terms of the percentage elongation and the Lankford value, as well as their corrosion behaviour. The examination of the processed steels form part of a research program that has the objective of developing ultra-low/carbon steels for automotive applications. Characterisation of the mechanical properties in terms of the percentage elongation and the average Lankford value was carried out for ultra-low carbon/Ti added steels from heats of 230 t of steel in the as-annealed condition. The results in terms of the above two parameters indicated the suitability of the experimental steels for extra-deep-drawing applications in the automotive industry. The corrosion behaviour shows that the microstructure does not have a strong influence on the electro-chemical behaviour of the evaluated steels when these are exposed to natural sea water. The average corrosion rate of the ultra-clean steel was about 0.0916 mm per year.

Keywords: Mechanical properties; Corrosion behaviour; Ultra-clean steels

1. Introduction

Several improvements have been carried out in the pellet workshop, in the direct reduction process, in steelmaking, in vacuum degassing, in ladle refining treatment and in the continuous casting of slabs, in the Mexican steel industry.

With regards to alloy composition, there has been a great improvement in steel-making practice in order to allow, for instance, the production of steels with low interstitial elements: carbon (C) and nitrogen (N); and with low sulphur and low phosphorus contents [1]. These steel-making improvements have allowed the possibility of producing ultra-clean steels for automotive applications.

This kind of vacuum degassed interstitial-free (IF) sheet steel has very high formability, especially for parts requiring good deep drawability [2]. High values of formability are achieved by reducing the interstitial element content (such as carbon (C) and nitrogen (N)) to very low levels by the steel-making route and/or by additions of stabilising elements such as titanium (Ti) or niobium (Nb) that combine with the N and C that is not removed by the steel-making practice [2,3]. Ultimately, the chemical composition of IF steels must be adjusted in order to satisfy the different requirements that demand these modern steels sheets.

High formability of ultra-low-carbon IF steels is associated [4] with the response of the ferrite matrix in heavily cold rolled IF sheet steels in recrystallizing during annealing to a polycrystalline structure with a strong $(111)\ \langle\bar{1}10\rangle$ recrystallization texture, producing high values of the average plastic strain ratio, $\bar{r}$. The deep-drawing characteristics of IF sheet steels, in terms of the measured Lankford value from a tensile test, are dependent strongly upon the development of strong $\{111\}$ recrystallization texture during in-line annealing [5].

Furthermore, during the process of removing interstitial elements by using micro-alloying elements, precipitates could be left in the matrix that may adversely affect the recrystallization process [6]. Ti left in excess in the matrix is far less effective [7] than Nb in retarding the recrystalliza-

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[*] Corresponding author. Tel.: +5-622-46-45; fax: +5-616-13-71.
E-mail address: julioalb@servidor.unam.mx (J.A. Juarez-Islas)

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tion process, but this characteristic is considered a distinct advantage in the design and processing of Ti-stabilised IF steel for extra-deep-drawing grades.

On the other hand, in [8–10] some insights on the effect of inclusions in steel were provided that accelerates its corrosion behaviour, showing that in the active state, the corrosion process occurs as a general form of attack. In circumstances where pitting corrosion has been a problem, it has been associated with a high local density of inclusions and with sulphur-rich regions of the matrix [11], but with the advent of modern steel-making practices producing low sulphur steels, much of this problem is already eliminated.

The aim of this work is to present results in terms of the mechanical properties and corrosion behaviour of three experimental heats of 230 t of ultra-clean carbon/Ti added steels after they have been hot rolled, coiled, cold rolled and annealed, and also to evaluate their corrosion behaviour when the steels are exposed to natural sea water.

2. Experimental procedure

The steel-making practice used to produce the experimental IF steels is according to established procedures that have been reported elsewhere [1]. The experimental heats were identified as U430/30119 (sample 1), U430/42229 (sample 2) and U430/40133 (sample 3), the chemical compositions of which are shown in Table 1.

The hot rolling of the slab specimens (0.01 m×0.05 m×0.10 m) was carried out in a Hilly mill of 50 t capacity. The rolling operation started with the specimen heated to 1250°C, a roll velocity of 0.24 m/s was employed, and the specimen was deformed to about 64% total reduction in two steps (0.035 m as the final thickness), finishing the hot rolling operation at 950°C. After hot rolling a coiling operation was simulated by cooling the specimen to 730°C, holding for 30 min at that temperature and then air cooling.

Table 1
Chemical composition of the sample of slab (wt.%)

Element	U430/30119 sample 1	U430/42229 sample 2	U430/40133 sample 3
C	0.004	0.005	0.005
Mn	0.098	0.085	0.11
Si	0.012	0.023	0.030
P	0.004	0.004	0.004
S	0.008	0.012	0.010
Al	0.031	0.042	0.071
Nb	0.001	0.003	0.000
V	0.001	0.000	0.001
Cu	0.01	0.010	0.015
Cr	0.000	0.000	0.000
Ni	0.012	0.008	0.013
Sn	0.001	0.000	0.001
N_2	0.003	0.0048	0.0044
Ti	0.061	0.075	0.069
B	0.000	0.003	0.000

Table 2
Determination of the Lankford value (r) and average Lankford value ($\bar{r}$)[a]

Lankford value	$r=\ln(w/w_0)/\ln(t/t_0)$
Average Lankford value	$\bar{r}=(r_{0^\circ}+2r_{45^\circ}+r_{90^\circ})/4$

[a] t_0 and w_0 are the initial thickness and initial width, respectively, and after deformation are denoted by t and w, whilst r_{0°, $2r_{45^\circ}$, and r_{90° are the Lankford values determined at 0°, 45° and 90° with respect to the rolling direction.

The cold rolling of the sheets were carried out in a Fenn mill of 25 t of capacity. The rolling operation was carried out at room temperature, a roll velocity of 0.20 m/s was used and the specimen was deformed to about 84% total reduction (0.003 m final thickness) in 11 steps.

The resulting sheets were annealed under an argon atmosphere at 800°C for 3 min. Specimens in all conditions were prepared using normal metallographic procedures and were etched with 2% Nital for microscopic observations and microanalysis. Tensile tests on annealed specimens were conducted on an Instron 1125 (10 t) testing machine, the specimens being machined according to the ASTM E-8 standard for flat specimens. From the results obtained from tensile test specimens in the annealed condition, the Lankford value was calculated for 0°, 45° and 90° with respect to the rolling direction, as shown in Table 2.

The behaviour of IF steels in the as-cold rolled and as-annealed condition was studied with regard to the corrosion resistance. For that purpose coupons of 0.050 m×0.050 m were electrically wired and embedded in an epoxy resin. The surface was ground with emery paper and then polished with alumina. The resulting specimens were washed and degreased. Then, the specimens were placed in a circular cell with recirculating natural sea water for 30 days, during the experiment a natural sea water flow of 20 l/h being kept constant. The potential was measured every day using a Bk-Tool-Kit 2703A and a reference electrode of calomel. During the experiments a water salinity of 36, a pH of 8 and a temperature of 25°C were kept constant. After the 30 days of testing, the steels were tested potentiodynamically using a Potentiostat/galvanostat Vimar PG-2EV which was connected a scanning generator. For the tests a calomel electrode was used as reference and graphite as contra-electrode and the IF steel was used as the working electrode. Natural sea water was used as electrolyte. The scanning was initiated at −1200 mV and finished at 300 mV, with a scanning velocity of 100 mV/min.

3. Results and discussion

Microstructural characterisation carried out on specimens in the as-cast condition showed that the main microstructure is formed of ferrite grains with some precipitates (<1 vol.%) of cuboidal-like morphology in the ferrite in the matrix. Identification of these precipitates was carried out by means of SEM microanalysis which showed that this precipitate is

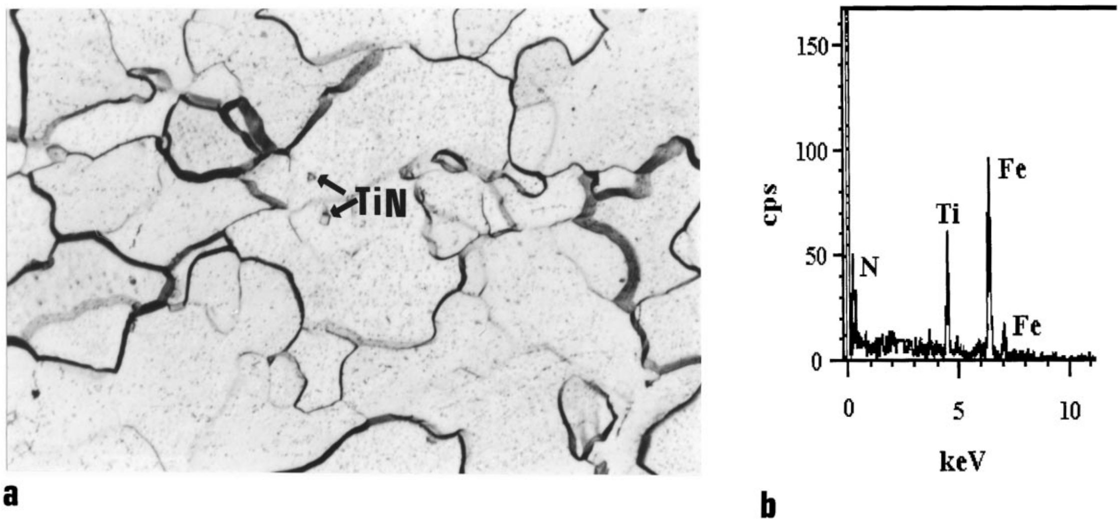

Fig. 1. Showing: (a) TiN precipitates of cuboidal-like morphology observed in ultra-clean steels in the as-cast condition (1000×); (b) SEM microanalysis of the TiN precipitates.

of the TiN type, as is shown in Fig. 1. After the re-heating (1250°C) and hot rolling (1250–950°C) of the slab specimens, apart from the ferrite grains and the TiN precipitate, the presence of precipitates of $Ti_4C_2S_2$ and TiS type was identified, as is shown in Fig. 2. As has been pointed out [12,13], in these special kind of steels several precipitates can be present such as TiN, TiS, $Ti_4C_2S_2$, MnS and TiC, the presence of these precipitates having a significant influence on the microstructure and its subsequent mechanical properties. In this study, the presence of TiN precipitates was identified (in the range 0.2–2 μm in size) in the as-cast condition and the precipitation of TiS and $Ti_4C_2S_2$ during the re-heating and hot-rolling operations of the specimens. Although TiN particles are stable, they can contribute to the precipitation reactions that occur during the reheating and hot-rolling operations by acting as nucleation sites for precipitates of the TiS and $Ti_4C_2S_2$ type, in agreement with several reports [14,15]. No further precipitation was observed in the as-cold-rolled (25°C) and annealed specimens (800°C, 3 min). Fig. 3a and b show representative microstructures of the ultra-clean steel in the as-cold rolled and annealed conditions, respectively.

From the mechanical properties achieved in the annealed specimens, Table 3 was obtained, which shows the resultant mechanical properties of as-annealed specimens at 800°C (3 min), in terms of 0.2% yield strength (0.2% YS), ultimate tensile strength (UTS) and percentage elongation El. (%), obtained in specimens tested at 0°, 45° and 90° with respect to the rolling direction. From the results obtained on tensile-tested specimens, the Lankford value was calculated for 0°, 45° and 90° with respect to the rolling direction, the average Lankford value for each specimen being shown in Table 4.

As can be observed from Table 1, the amount of Ti added to the steels was 0.061, 0.075 and 0.069 (wt.%) for specimen 1, 2 and 3, respectively. From Table 3, it can be seen that specimens annealed at 800°C showed values of elongation of 61.2, 64.5 and 68.4 perpendicular to the rolling direction, of 75.3, 72.0 and 62.3 diagonally to the rolling direction and

Table 3
Mechanical properties of ultra-clean steel stabilised with titanium in the as-annealed condition (800°C, 3 min)

Steel	0.2% yield strength (MPa)	UTS (MPa)	Elongation (%)
(a) 0° with respect to the rolling direction			
Sample 1	152.6	294.7	55.59
Sample 2	138.5	254.3	61.74
Sample 3	167.1	306.4	56.68
(b) 45° with the respect to the rolling direction			
Sample 1	145.3	310.6	75.25
Sample 2	141.8	298.5	71.95
Sample 3	156.5	294.7	62.29
(c) 90° with respect to the rolling direction			
Sample 1	137.0	288.2	61.19
Sample 2	140.5	293.5	64.48
Sample 3	153.5	305.9	68.44

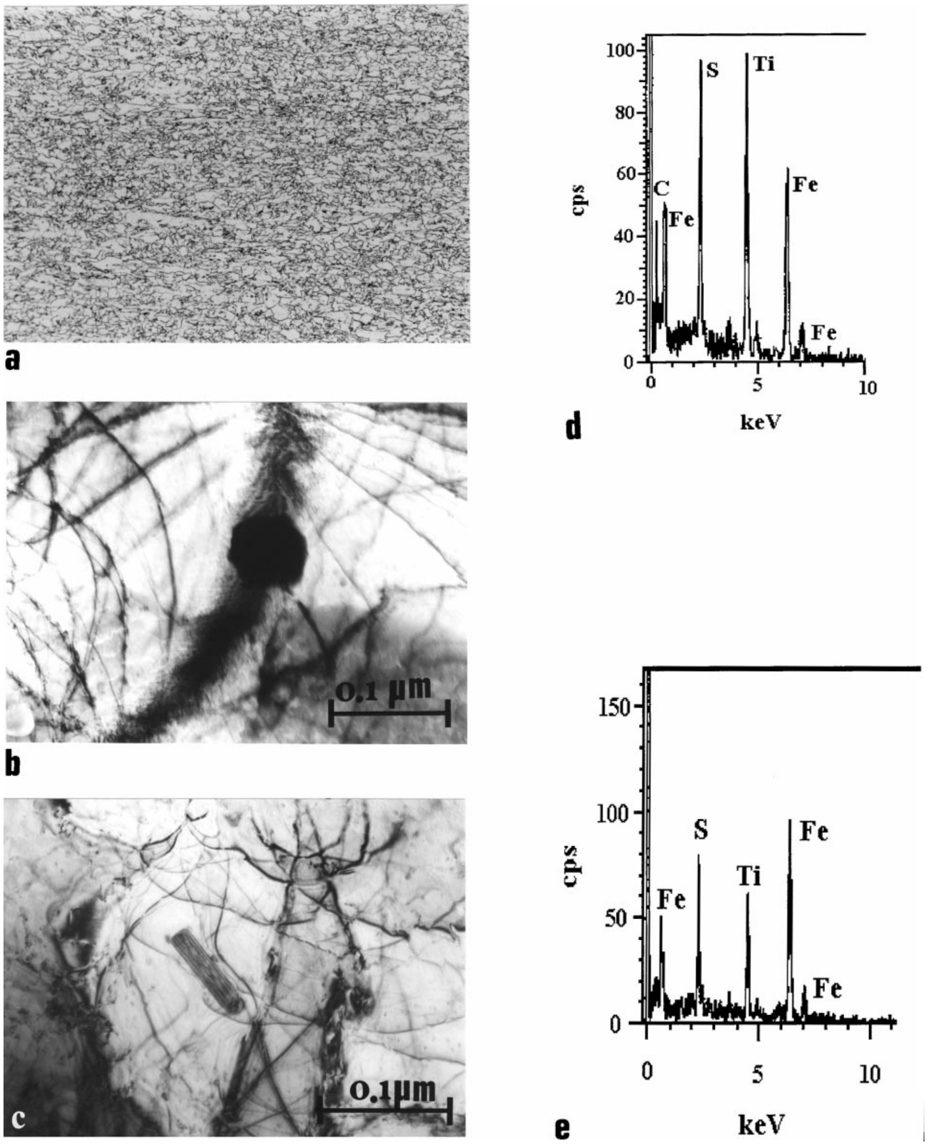

Fig. 2. Showing: (a) representative microstructure of ultra-clean steels in the as-hot rolled condition (100×); (b) $Ti_4C_2S_2$ precipitates of hexagonal-like morphology; (c) TiS precipitates of elongated morphology; (d) SEM microanalysis $Ti_4C_2S_2$ precipitate; (e) SEM microanalysis TiS precipitate.

of 55.6, 61.7 and 56.7 parallel to the rolling direction, for specimens 1, 2 and 3, respectively. As has been pointed out [2], cold-rolled sheet steels have been classified by their average Lankford value ($\bar{r}$) and total elongation in four degrees, as is shown in Table 5, and due to stringent customer requirements, a new grade has become in demand for which the formability value and total elongation will be higher than 2.0 and 50%, respectively. To achieve these mechanical properties, it is recommended to anneal the cold-rolled sheets at temperatures of 800°C and above. In the evaluated annealed steels sheets, the total value of elongation obtained in specimens tested at 0°, 45° and 90° was found to be higher than 55% and the $\bar{r}$ value was between 2.02 and 2.14, indicating the suitability of the experimental steels for extra-deep-drawing applications.

Table 4
Lankford values (r) determined at 0°, 45° and 90° with respect to the rolling direction and the average Lankford values $\bar{r}$ for processed ultra-clean steels

Lankford values	Sample 1	Sample 2	Sample 3
r_{0°	2.07	2.19	2.03
r_{45°	2.01	2.05	2.00
r_{90°	2.34	2.28	2.07
$\bar{r}$	2.10	2.14	2.02

The influence of annealing temperature on the $\bar{r}$ value has been discussed [16] in terms of the volume fraction of γ transformed during annealing in the range of temperature 775–975°C. This is mentioned because ultra-low-carbon steels have a narrow $\alpha+\gamma$ temperature; the $\alpha\rightarrow\gamma$ transformation finishes in a brief period; and the $\bar{r}$ value increases as the temperature increases, achieving a maximum close to the

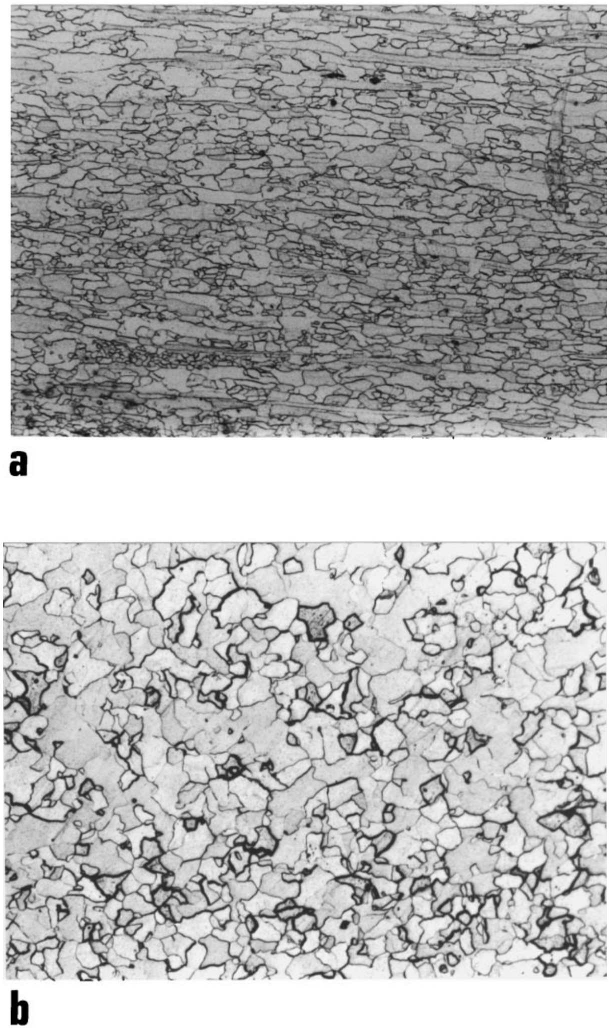

Fig. 3. Representative micrograph of ultra-clean steels: (a) in the as-cold rolled condition (100x), and (b) in the annealed condition (500x).

Ac_3 temperature, and after that decreasing abruptly when annealing is carried out in the γ region. The values of $\bar{r}$ achieved in this study are similar to those reported in [16], when the specimens were annealed at 800°C.

On the other hand, the behaviour of IF steels in the as-cold-rolled and as-annealed condition was studied with regard to corrosion resistance. The curves of potential versus time were obtained from daily measurements of potential with respect to a saturated calomel electrode. The curve of potential versus time for the IF steel in the as-annealed condition in shown is Fig. 4a, where it can be observed that during the first few days of the test, there is an activation of the surface that is in contact with the electrolyte, showing values close to −765 mV during the first day of the test, then the values of potential moving to −758 mV (2 days), −747.5 mV (3 and 4 days), −745 mV (5 days), −750 mV (6 days), −745 mV (7 days), −740 mV (8 days), after which the potentials are shown to be stable until the end of the test (−740 to −760 mV). This stability behaviour of the potential can be due to the formation of a thick layer of corrosion products that prevent an ionic interchange with the media, because when the corrosion products were removed from the steel surface, a shiny surface was observed.

The curve of potential versus time for the IF steel in the as-cold rolled condition in shown in Fig. 4b where it can be observed that during the first day of the test, there is an activation of the surface that is in contact with the electrolyte, showing values close to −771 mV during the first day of the test, then the values of potential moving to −749 mV (3–6 days), −737.5 mV (8 days), −758 mV (9 days), after which the potentials are shown to be stables until the end of the test (−740 to −771 mV). Once again the stability behaviour of this steel in terms of the potential is attributed to the formation of a thick layer of corrosion products.

The potentiostatic tests carried out in the steels in both the as-cold-rolled and as-annealed conditions showed that the potential of corrosion for the steel in the as-annealed condition (Fig. 5a) was close to −871 mV. The cathodic region shows a behaviour that is governed by activation, without presenting a current limit apparent. In the anodic region (between −700 and −400 mV), a poor tendency to passivation was observed, showing later a trans-passitivity region. The corrosion potential of the steel in the as-cold-rolled condition (Fig. 5b) was −745 mV. As in the annealed coupon, a poor tendency to passivation was observed, showing later a trans-passivity region. Between −850 and −800 mV, for the cathodic region, it was possible to observe a different mechanism, i.e. after presenting a cathodic behaviour dominated by activation, a region is presented that is governed by oxygen diffusion.

At the end of the exposure test, a reduction in the corrosion potential (−900 mV) was observed in both specimens, being more severe for the steel in the as-annealed condition. In both cases, the polarisation curves show in the cathodic region a process dominated by activation, with this mechanism continuing into the anodic region, which indicates that after a exposition time in natural sea water, the tendency to show a particular passivity is lost. It was expected that the steels would show a different behaviour in terms of corrosion resistance, because the as-cold rolled coupon contained elongated ferrite grains that are thermodynamically more unstable as compared with the recrystal-

Table 5
Classification of ultra-clean steels in terms of the percentage elongation and the average Lankford value

Properties	Commercial quality	Drawing quality	Deep-drawing quality	Extra-deep-drawing quality
El. (%)	36.9–42.2	40.0–45.0	42.7–47.5	46.1–50.5
$\bar{r}$	1.00–1.41	1.23–1.51	1.42–1.84	1.73–2.12

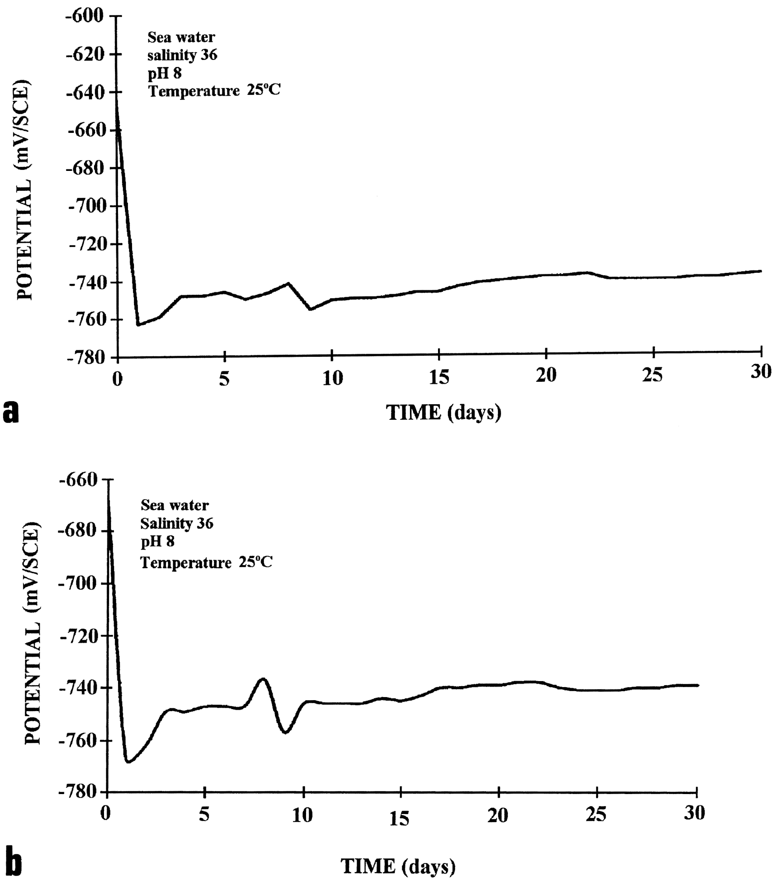

Fig. 4. Curves of potential versus time for ultra-clean steels: (a) as annealed; (b) as-cold rolled.

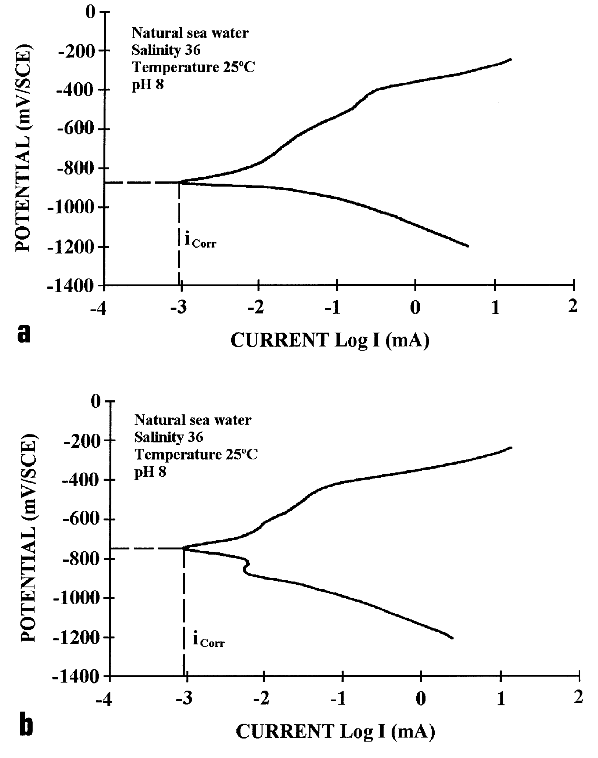

Fig. 5. Curves of potential versus current for ultra-clean steels: (a) as-annealed; (b) as-cold rolled.

lized ferrite grains of the steel in the as-annealed condition: however, it is apparent that the microstructure does not have a strong influence on the electrochemical behaviour of the steel when this is exposed to natural sea water. The average rate velocity of the IF steels in both conditions was about 0.0916 mm per year.

4. Conclusions

1. The main microstructure obtained in as-cast ultra-clean steels was of the ferrite type with some precipitates of TiN. After the re-heating and the hot-rolling operations, the presence of TiS and $Ti_4C_2S_2$ precipitates was detected.
2. The resulting mechanical properties of ultra-clean steels processed according to internal standard procedures, and after being hot rolled, coiled, cold rolled and annealed, showed an outstanding behaviour in terms of the percentage elongation and the Lankford value, achieving values that allow the resulting annealed sheets to have commercial applications in extra-deep-drawing applications.
3. In terms of corrosion behaviour, it is apparent that the microstructure does not have a strong influence on the electrochemical behaviour of the evaluated samples of steel when these are exposed to natural sea water. The

average corrosion rate of the ultra-clean steels was ≈0.0916 mm per year.

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