Ion - nitriding of austenitic stainless steels

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Abstract

The characteristics induced by ion-nitriding on AISI 316 stainless steels are evaluated in function of treatment times and temperatures, in a field of values permitting the optimization of post-nitriding resistance to corrosion. The electrochemical behaviour of the nitrided layers is correlated with their morphology. Under particular treatment conditions, a corrosion resistant layer, constituted by a new ε' tetragonal phase of the $(Fe,Cr,Ni,Mo)_2N_{1-x}$ type, is produced. Since this phase is obtained under conditions of metastability, an assessment is made of the influence of the treatment cycle and the amount of Mo in the alloy (indispensable for the formation of ε') on the layers constitution.
The corrosion tests carried out using chloride solutions as aggressive medium, show that nearly the same behaviour of the base alloy is attained only if the nitrided layer is mainly constituted by ε' phase.

Riassunto

Le caratteristiche indotte dalla nitrurazione ionica di acciai inossidabili tipo AISI 316 sono valutate tenendo conto dell'influenza dei tempi e delle temperature di trattamento. La variazione di questi parametri è seguita in un campo di valori che consentano di ottimizzare le caratteristiche di resistenza alla corrosione del materiale dopo nitrurazione. In tal senso il comportamento elettrochimico degli strati nitrurati viene correlato con la loro costituzione, che, in particolari condizioni di trattamento, è caratterizzata dalla preponderante presenza di una nuova fase tetragonale, indicata come ε', del tipo $(Fe,Cr,Ni,Mo)_2N_{1-x}$. Poiché ε' si forma in condizioni di metastabilità, viene valutata l'influenza del ciclo di trattamento e del tenore di molibdeno in lega, la cui presenza è indispensabile affinché ε' possa formarsi, sulle caratteristiche indotte dal trattamento.

Introduction

Nitriding of ferrous alloys has been a long-standing research topic in our Department. From the application standpoint, ion-nitriding is one of the most attractive surface heat treatments on account of its markedly brief cycle time and suitability for computerised control.

Another point in favour of the adoption of this technique is that it can be employed for stainless steels because the passive layer is removed by the treatment itself.
Data on the characteristics of the layers formed on such alloys abound in the literature (1-6). Particular attention has been directed to their growth kinetics (7,8).
Corrosion resistance (9,10) is an especially significant aspect of the application of nitriding, since this parameter is of prime importance in assessing the behaviour of stainless steels.

Nitriding, in fact, leads to an improvement in the wear resistance of stainless steels. Against this, however, must be set a heavy reduction of the degree of nobility of the alloy, marked by a significant fall in the free corrosion potential (6). Among the alloys subjected to this type of treatment, AISI 316 displayed a particularly interesting behaviour, since after the particular nitriding conditions described in this paper, its corrosion resistance was still comparable to that of the base alloy. The AISI 304 stainless steel behaves in different way, because the absence of molibdenum in the alloy does not allow the formation of monophasic ε' layer, as discussed below.
Furthermore it must be pointed out that, while the austenitic stainless steels, especially the AISI 304,

could be sensitized at nitriding temperatures in function of the treatment time, in our nitriding tests on AISI 316 stainless steel we have not observed any sensitization phenomena, according to the results reported in the literature. In fact, for an AISI 316 type steel, containing 0,03% C and 2% Mo, it was noted (11) that, in the range 400-700 C, the susceptibility to sensitization increases with increasing temperature, but, for treatment at about 500 C, the sensitization could occur after one million of seconds (about 300 h), and for treatment at 600 C, after one hundred thousand seconds (about 30 h).

This paper reports the results obtained with stainless alloys, belonging to this family with substantial differences in molybdenum content, whose role is fundamental, in order to obtain ε' layers.
Therefore the influence of this parameter and the influence of significant variations in nitriding temperatures and times on the behaviour of these alloys have been evaluated.

Experimental methods

Ion-nitriding was performed in a Klockner Ionon industrial type furnace at a working pressure of 500 Pa in an atmosphere ensured by a flow of N_2 and H_2 at 10 and 30 m^3/h respectively.
The process usually lasted 40 h, i.e. 28 h at 500 C followed by a treatment of 12 h at 400 C. In some cases, the first phase was carried out at 500 C or 600 C for 28 h, followed by a treatment of 2 h at 400 C (Table I).
The specimens were taken from AISI 316 austenitic

TABLE I - Heat treatment cycles

Heat Treatment	Time	1° step			2° step	
	t (h)	T (C)	t (h)		T (C)	t (h)
A	40	500	28		400	12
B	30	500	28		400	2
C	30	600	28		400	2

TABLE II - Chemical composition (weight %) of the austenitic stainless steels

	C	Ni	Cr	Mo	Si	Mn	N
AISI 316 (I)	0.038	12.85	18.80	2.93	0.42	1.73	—
AISI 316 (II)	0.036	11.70	17.52	2.01	0.50	0.93	—
316 Type, 4% Mo	0.041	13.24	16.74	4.07	0.41	1.39	0.13

stainless steel sheets at finishing stage 2 B (pickling followed by final cold-rolling). The sheets were taken from two different pours. Their analyses are shown in Table II. A steel with a non-standard composition was also ion-nitrided; this was very similar to AISI 316, except for its appreciably higher molybdenum content.

Nitriding tests were also performed in a tubular lab furnace in an ammonia flow, using Fe and Ni powders coprecipitated from oxalates, as reported elsewhere (12), powdered AISI 316 and 100 μm thick AISI 316 sheets. The nitriding process consisted of a treatment of 6 h at 500 C, followed by 20, 90 or 180 h at 380 C. By means of X-ray analysis (Fe K_α radiation, λ_{α_1} = 0.19373 nm) the phases present in the nitrided layers were determined.

Microstructural analyses were carried out after nitriding with both an optical microscope and a scanning electron microscope coupled to an energy dispersion microprobe. Auger analyses were also made on some of the AISI 316 specimens.
Surface microhardness was evaluated with a Knoop penetrator, using a 50 g test load.
The electrochemical behaviour of the layers was evaluated.

Their corrosion rates were calculated from weight loss measurements after immersion in 0.1 N NaCl solution, at 25 C, for 15 to 75 days, and polarization curves were recorded in the same environment.

Experimental results

Particular treatment cycles can be used to form layers

with a strong predominance of a particular phase, especially on Mo-alloyed austenitic stainless steels. This phase has been recognised as structurally very similar to the tetragonal nitride FeNiN (6,10,13). It has been assigned the formula $(Fe,Cr,Ni,Mo)_2N_{1-x}$ and the symbol ε', because its N content varies over a wide range like that of the exagonal phase ε (Fe_2N_{1-x}) of the Fe-N system.

The ε' phase displays a composition range extending to very low nitrogen contents (about 20% atomic), i.e. even less than those of ε. Despite its structural analogies with FeNiN, the formation of ε' is certainly not solely due to the presence of Ni in the alloy, since it would otherwise be encountered on AISI 304 (it has not been recognised on these nitrided alloys) (6), but to the particular effect of Mo, namely the distinguishing feature of this class of steels.

Careful investigation resulted in definition of the composition field and evaluation of variation of the lattice constants of ε' in function of the N content. It was not possible to prepare ε' specimens by nitriding in an ammonia flow of very tiny fragments of stainless steel or powders with the corresponding composition obtained by precipitation of suitable solutions followed by reduction, and then carry out their chemical analysis.

All that could be done was to examine the thin sheets after the treatment described.
Layers about 70 μm thick were built.
X-ray and SEM quantitative analyses of the surface of ion-nitrided samples, after successive removal of material by lapping, allowed us to calculate the lattice constants of the ε' phase in function of the composition, as shown in Fig. 1.
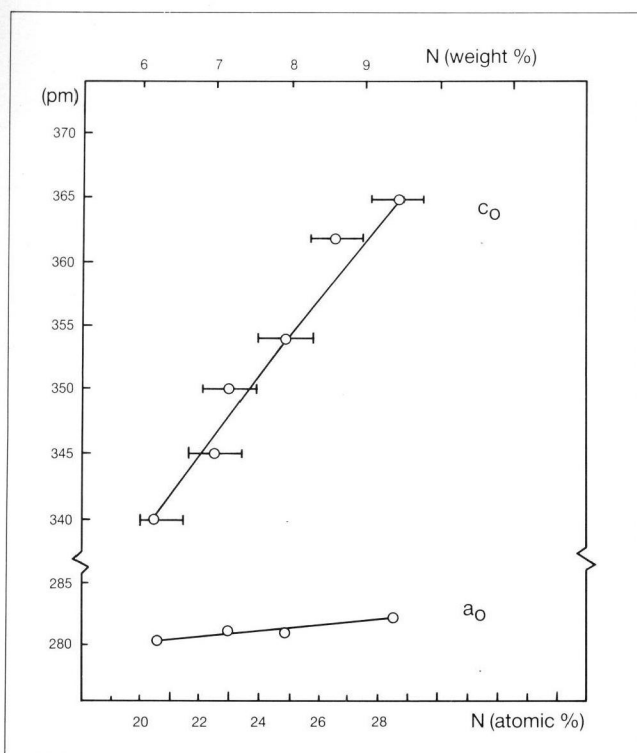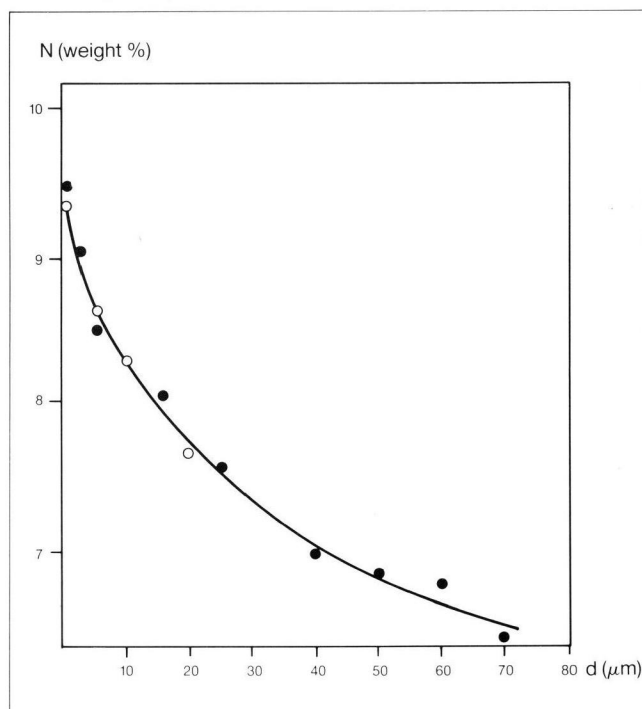
Fig. 1 - Lattice constants of the phase ε' vs. N content.

Fig. 2 - Nitrogen content of ε' phase vs. distance from the surface; (●) values calculated from the measured lattice constants of ε'; (○) values measured by means of Auger analysis.

The lower limit of composition of ε' reaches almost 20% atomic nitrogen content (about 6% by weight). Furthermore it must be noted, as illustrated in Fig. 2, that the nitrogen content decreases with the distance from the surface.

There can be no doubt that it is indeed the greater trend towards low N contents at 400 C of the ε' field as opposed to the ε field that leads to the formation after ion-nitriding of AISI 316, followed by treatment at 400 C, of a substantial monophasic layer even with N contents corresponding to compositions that lie in the triphasic γ' + ε + CrN field (14) at 500 C.

It must be noted that, at this temperature, a nitrogen content high enough to produce monophasic ε layers cannot be obtained, because of the insufficient nitriding power of the treatment medium. The cristalline lattices of γ' and ε' show noticeable structural analogy.

The elementary γ' cell reported in Fig. 3 (f.c.c. with one N atom in position 1/2 1/2 1/2) is, in fact, matched by an analogous pseudo cell ε', in which N atoms are partially placed also at the center of the four sides, with a statistical distribution.
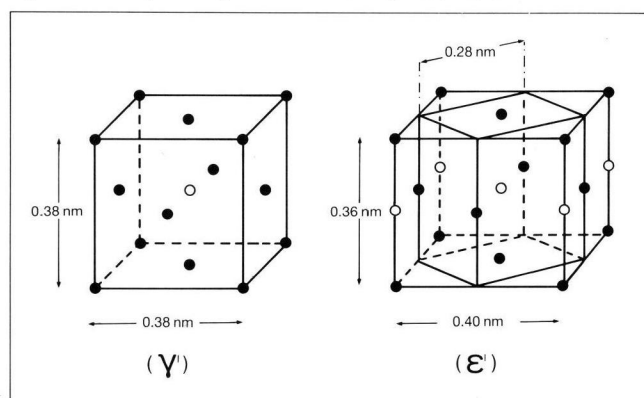By analogy with what takes place in the case of FeNiN, this brings about a small deformation of the original cell (slight increase in a_o and corresponding contraction of c_o).
The true tetragonal elementary cell ε' displays a lattice constant $a_o = a/2 \cdot \sqrt{2}$, whereas constant c_o remains the same (Fig. 3).

The lattice constants observed vary in function of the degree of nitriding in the range:

$a_o = 0.2800$ nm; $c_o = 0.3398$ nm
$a_o = 0.2818$ nm; $c_o = 0.3660$ nm

Fig. 3 - Elementary cells of γ' (f.c.c.) and ε' (tetragonal) phases.
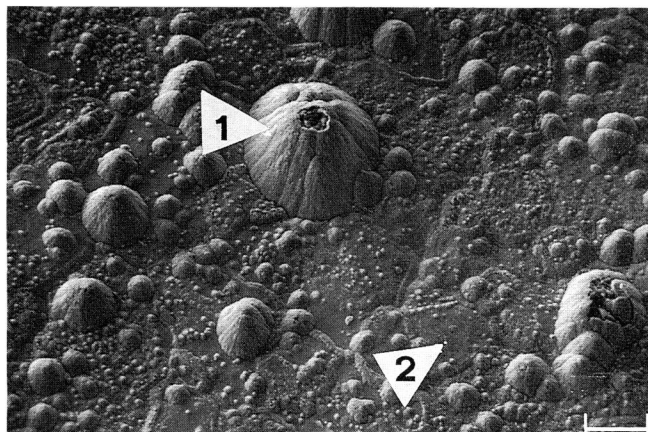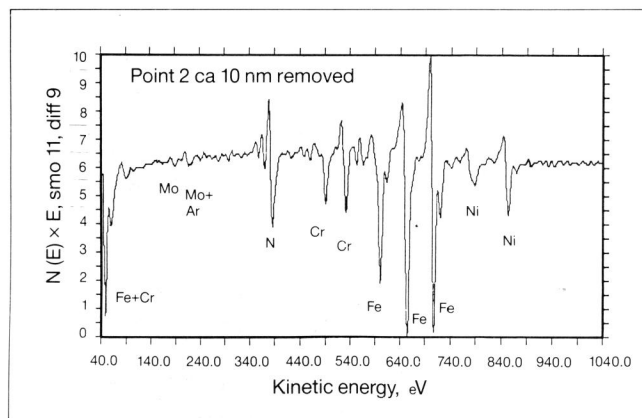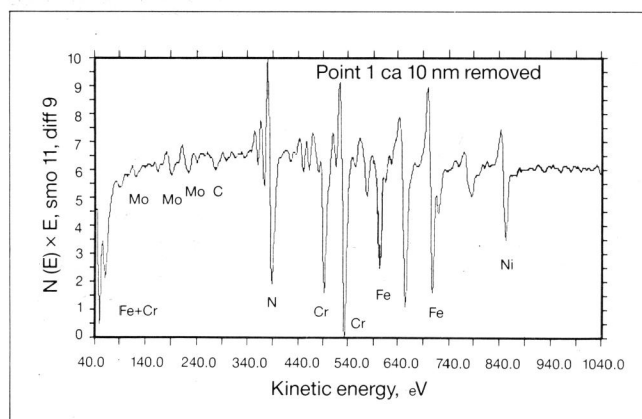

(γ')   (ε')

Fig. 4 - Ion-nitrided AISI 316 (I) stainless steel (treatment B): SEM photograph of the surface.

Fig. 5 - Auger spectra of ion-nitrided AISI 316 (I) stainless steel (treatment B); (a) referred to point 1 in Fig. 4, (b) referred to point 2 in Fig. 4.

Auger analyses revealed the variation of the N content and alloy elements in the nitrided layers. As can be seen in Fig. 2, the N content results are in close

agreement with those derived from X-ray and SEM methods. It should be remarked that these analyses were performed on various samples prepared by successive removals of part of the nitrided layer from the original surface. On approaching the matrix (removal of 5 to 20 µm), there is a fall in N content comparable to that deduced from evaluation of the shift of the diffraction peaks of the nitrided phases on the diffractograms.

No significant changes in alloy element concentrations were noted in the layer, in keeping with its substantial monophasicity.
In fact the protuberances, Fig. 4, observed on the surface, show marked N, Cr and Mo enrichment, compared with the layer, as clearly evidenced by the Auger spectra of Fig 5 (a,b).

Only on the surface little amounts of different phases can appear.
It can thus be concluded that these nitrides, not detected by X-ray analysis, are of the (Cr,Mo)N type.

Layer evolution on temperature

A prolonged treatment at 400 C causes the conversion of phase ε' into more stable phases in proportions dependent on the nitriding level attained; the sensitivity of this conversion increases in function of time. What is said below about the thickness of the nitrided layer is also relevant in this context.

After 12 h treatment ferrite also appears, as a result of substraction of alloy elements following the formation of the various nitrides. It should be noted that during this low-temperature stage of the cycle, the effect of ion implantation is negligible and hence the system is not disturbed in its progress towards thermodynamic equilibrium.

As far as the stability of phase ε' is concerned, similar considerations apply to type (II) samples (lower Mo content) subjected to the same treatment schedules. Here, however, the limited diffusion of N, evidenced by a thinner layer, leads to the formation of larger quantities of ε', so much so that protracted treatment at 400 C results in a considerable formation of ε, whereas in the previous case γ' was the predominant phase.

The influence of the temperature during the first part of the cycle, i.e. at 600 C (treatment C), enabled the presence of ε', while considerable amounts of CrN were detected in the whole layer and not only on the surface, as observed after the treatment B.

It should be noted, in fact, that the higher nitriding temperature provokes a substantial precipitation of very stable Cr nitrides.

The totality of these findings enables the role played by Mo as an alloy element to be defined as follows. Since phase ε' is unable to form on AISI 304 steel, it may be concluded that the small amount of Mo capable of passing into solid solution in this phase initially promotes its formation. As stated earlier, the field of composition of ε' extends to N values well below those noted for phase ε (10,11) and certainly to much higher Cr and Ni values (15).

The fact that a protracted treatment at 400 C leads to a gradual fall in ε' content to its disappearance and replacement by $\varepsilon + \gamma' + CrN$ mixtures suggests that the formation of ε' takes place under conditions of thermodynamic metastability starting from phases generated by ion implantation, and hence with marked structural imperfections.

Mo values of the order of 2% to 3% appear to boost the formation and continued existence of ε', even after residence at 400 C for several hours. By contrast, higher Mo values have a negative effect on the presence of ε' and accelerate the decomposition process on account of the concomitant stabilising effect on the (Cr, Mo)N nitride.

CrN type phases were present, even well down in the layer, when the higher Mo stainless steel was treated. When the Mo content is around 4%, the layer is so enriched in (Cr, Mo)N type nitrides as to make the formation of ε' more difficult. This phase, what is more, possess a certain degree of metastability, as indicated

Fig. 6 - Microhardness profiles of samples ion-nitrided (treatment A); (●) AISI 316 (I); (○) AISI 316 (II); (□) 316 type, 4% Mo.
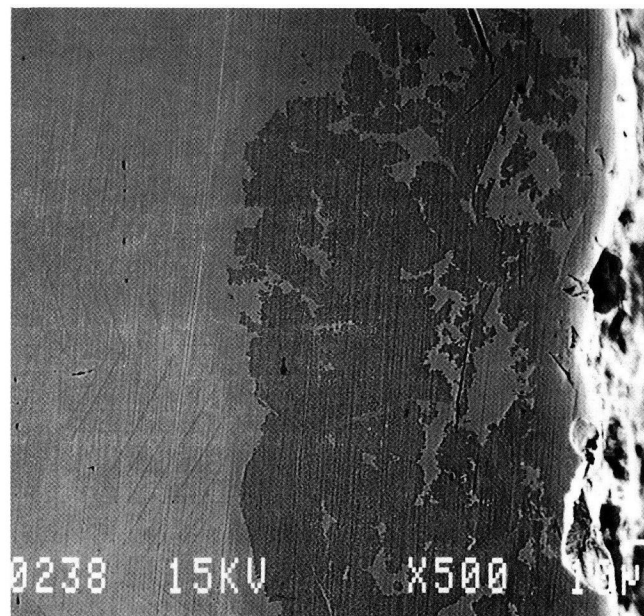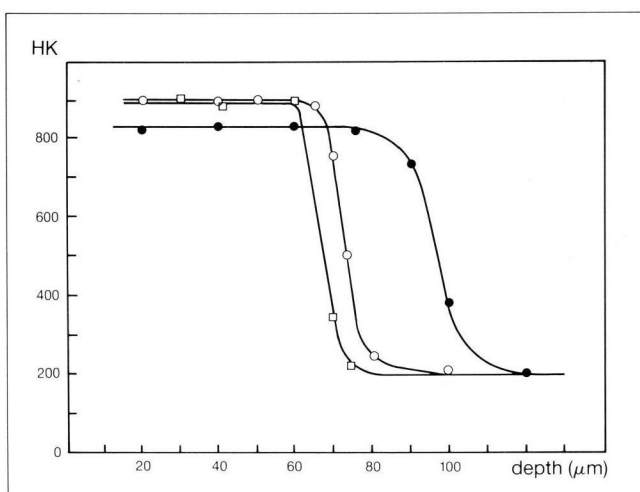

Fig. 7 - Ion-nitrided 316 type, 4% Mo stainless steel (treatment A): SEM photograph of a cross-section (Nital etching).

by the influence of the time of treatment at 400 C on their permanence in the nitrided zone.

In Fig. 6 the microhardness profiles of nitrided layers obtained with treatment A on the three base alloys under study are reported. They were measured with the aid of a Knoop - type penetrator so as to have more significant results in view of the shape of the imprint.

Approximately the same hardness values were measured on AISI 316 (II) samples and on the high molybdenum stainless steel, while slightly lower values were obtained on AISI 316 (I) samples together with noticeably thicker layers.

In fact on AISI 316 (I) samples, after treatment A, a diffusion phenomenon increases the layer thickness up to levels of at least 80 or so micrometers. From these results it can be deduced that, on the assumption of parity in the overall N content, diffusion provokes a change in surface N concentration with a low decrease of hardness values.

This fact can explain the tendency of this sample to evolve towards γ' rather than ε nitrided phases for a long treatment at 400 C.

In Fig. 7 a layer formed on AISI 316 type Mo steel, after treatment A, is visible. Its polyphasicity is rendered evident by the electrolytic etching.

Microprobe analysis of the phases reveal an impoverishment of Cr and Mo in the light phase. This result together with the higher microhardness values

with respect to the dark phase, can be associated with the presence of γ'.

Electrochemical behaviour

Table IV lists the corrosion rates of various samples in function of increasing time of immersion in NaCl 0.1N solution.

The best behaviour is clearly displayed by AISI 316 (I), which, after treatment B, has a virtually single phase nitrided layer. As stated in previous works (6,10), the monophasic ε' layer alone shows a corrosion resistance quite similar to the one of the base alloy.

Whereas the samples of AISI 316 (I), AISI 316 (II) and 316 type, 4% Mo, after treatment A, show higher corrosion rates, in keeping with the corresponding morphologies of the layers, see Table III.

The polyphasicity of the nitrided layer can create short-circuited microgalvanic elements, thus enhancing the corrosion of the less noble phase.

The polarization curves recorded in the same environment, NaCl 0,1N, can provide additional information. However it must be beared in mind that a strict correlation with the weight loss measurements cannot always be found, because these electrochemical tests have been carried out after only 15 minutes of immersion in the aggressive medium, while corrosion tests require long immersion periods.

In the case of AISI 316 (I), Fig. 8 (a), after treatments A and B low current densities are obtained on the both layers. It is not possible to observe, in these tests the improvement of corrosion resistance due to ε' phase.

The polarization curves for AISI 316 (II), after treatment A and C are visible in Fig. 8 (b).
The cathodic and anodic current densities are one order of magnitude greater than on AISI 316 (I).

In particular the curves relative to treatment C make it clear that cleaning the surface after nitriding causes drastic changes in electrochemical behaviour. Very slight removal of material is enough to bring about a marked shift of the free corrosion potential to more negative values, resulting in a decidedly less passivable layer.

The more positive potential values are attributable to the presence of extremely thin layers containing only Cr nitrides and thus devoid of protective capacity with respect to the base alloy.

Finally the polarization curve for the 316 type high molybdenum steel, Fig. 8 (a), shows a low tendency to passivation of these nitrided layers.

TABLE III - Phases present in the nitrided layers

Stainless steels	Heat Treatments			Phases		
		ε'	γ'	CrN	α	ε
AISI 316 (I)	A		+ + +	+ + +	+	
AISI 316 (I)	B	+ + + +		tr		
AISI 316 (II)	A	+ + +	+ + +	+		+ +
AISI 316 (II)	C	+ + + +		+ +		
316 type, 4% Mo	A		+ + +	+ + + +		

TABLE IV - Corrosion rates in NaCl 0.1N,T = 25C, of ion-nitrided stainless steels

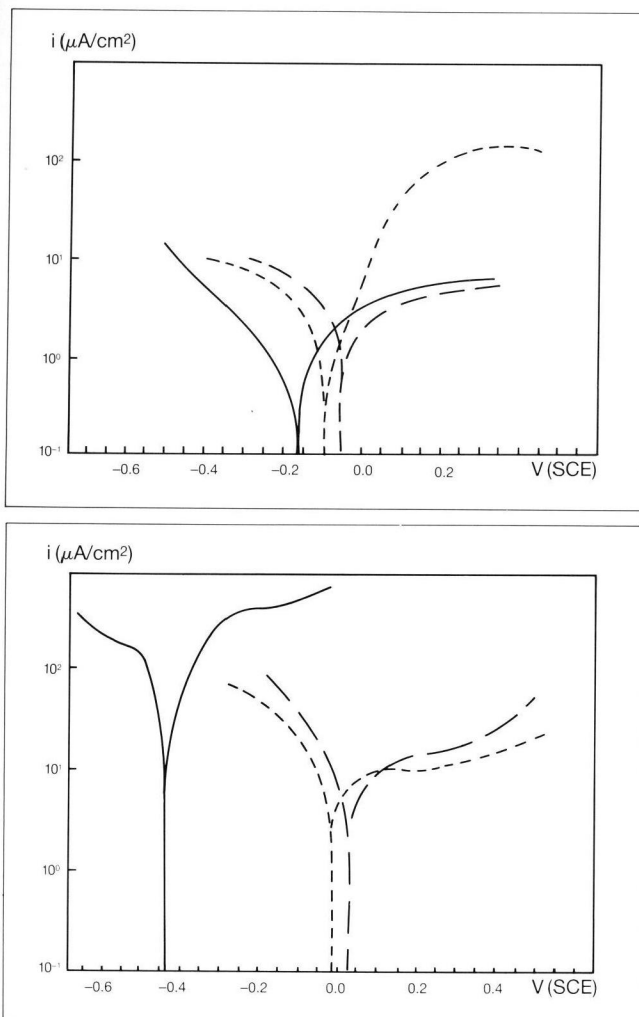| Samples	Heat Treatments	Corrosion rates (g/dm^2 day) Immersion time (days)		
		15	30	75
AISI 316 (I)	A	0.010	0.010	0.009
AISI 316 (I)	B	0.0005	0.0005	0.0005
AISI 316 (II)	A	0.006	0.005	0.010
AISI 316 (II)	C	0.0008	0.0008	0.0008
316 Type, 4% Mo	A	0.010	0.007	0.005

Fig. 8 - Polarization curves in 0.1 N NaCl solution at 25 C recorded on ion-nitrided samples. (a): (— —) AISI 316 (I), treatment A; (—) AISI 316 (I), treatment B; (– – – –) 316 type, 4% Mo, treatment A. (b): (– – – –) AISI 316 (II), treatment A; (— —) AISI 316 (II), treatment C; (—) AISI 316 (II), treatment C, after slight lapping.
Potential scan rate: 1 mV/s.

Conclusions

The results obtained on austenitic stainless steels (AISI 316 type) heat treated by means of different ion-nitriding cycles are the following:

— a new tetragonal phase ε' of the type $(Fe,Cr,Ni,Mo)_2N_{1-x}$ is obtained by nitriding at higher temperature, 500 C, followed by a brief permanence at 400 C, if the molybdenum content is about 2%.

— higher molybdenum values in the alloy have an adverse effect on forming a surface layer almost entirely composed of phase ε', because of the contemporary presence of (Cr,Mo)N type nitrides.

— protracted heating at 400 C decrease the ε' content in the layers; this phase must therefore be regarded as being formed under conditions of thermodynamic metastability, starting from phases formed by means of ion implantation and hence with marked structural defects.

— after usually employed ion-nitriding treatments a noticeable decrease of the corrosion resistance of the surface is observed, while, when nitrided layers are essentially constituted by ε' phase, their corrosion resistance is similar to the one of the base alloy. In the other cases the corrosion rates are higher by one order of magnitude.

— Finally it must be noted for the steels used in corrosion tests that the time treatment at high temperature was noticeably shorter than the sensitization time of the base alloys.

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