Relationship Between the Electrochemical and Corrosion Behavior and the Structure of Stainless Steels Subjected to Cold Plastic Deformation

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ABSTRACT

The present investigation forms part of a systematic study about the influence of cold plastic deformation on the electrochemical and corrosion behavior of metallic materials, with the aim of determining and elucidating such aspects of their behavior and correlating them with the microstructural effects of the deformation, these being analyzed by metallographic and x-ray techniques and by transmission electron microscopy. In this respect, the influence of cold plastic deformation on the electrochemical and corrosion behavior of two stainless steels (AISI 304 L and 316 L) in different aggressive media (with and without chloride ions) has been studied with reference to the following points: (i) deformation type, *i.e.*, tensile stress, cold drawing, or cold rolling, and conditions, *i.e.*, at room temperature and at $-196^{\circ}C$; (ii) relative orientation of the exposed surface with the deformation direction, *i.e.*, parallel and perpendicular; (iii) texture, defects, and martensite transformation.



Fig. 1. Test cell (cross section)

The study of the influence of cold plastic deformation on the electrochemical and corrosion behavior of austenitic stainless steels was carried out in our Institute mainly because of the need for a systematic collection of data as a basis for a more reliable utiliza-

* Electrochemical Society Active Member. ¹ Present address: Centro Informazioni Studi Esperienze (CISE), Milano, Italy. tion of these materials which are often used in the work-hardened state. The correlation between the electrochemical behavior and the structural effects produced by cold plastic deformation, *i.e.*, texture, surface



Fig. 2. Cathodic polarization curves for hydrogen evolution on AISI 304 L steel in deaerated 1M H₂SO₄ solution at 25°C for different values of the deformation degree (indicated as a percentage). Deformation by rolling at both room and liquid N₂ temperature; long transversal (T_L) section. Potential values are relative to a standard mercury sulfate electrode (SSE).

Milano, Italy. Key words: corrosion, austenitic stainless steels, cold plastic deformation, martensite transformation, passivity, pitting, surgical plants.

Table I. Chemical composition and some structure characteristics of the studied stainless steels (in the as-received state, *i.e.*, after solution heat-treatment)

Austenitic stainless steel	Subsequent cold working	С	Si	Weig Mn	t perc P	cent con S	mpositi Cr	on Ni	Мо	N	ÁSTM mi- crograin size number	M _{d30} a (°C)	М₅ ^ь (°С)	δ-ferrite (%)	Dislocation density (10 ⁹ cm/cm ³)
AISI 304 L	Tension Rolling	0.025	0.45	1.39 1.40	0.023	0.021 0.013	18.60 18.10	8.75 10.30	0.50	0.036	$6 \div 6.5 \\ 4 \div 4.5$	+ 22 + 18	<-196 <-196	$0.1 \div 0.2$	$\begin{array}{c} 1.30 \pm 0.63 \\ 0.96 \pm 0.21 \\ 1.17 \pm 0.65 \end{array}$
AISI 316 L	Drawing Rolling	0.022 0.023 0.026	0.43 0.40 0.41	1.31 1.45 1.24	0.033 0.034 0.008	0.023 0.011	16.60 16.10	10.65 10.90 10.90	2.90 3.00 2.20	0.033 0.037 0.034	5.5 $4 \div 4.5$	-14 - 17 + 7	< -196 < -196 < -196	0	1.17 ± 0.65 1.02 ± 0.28 1.59 ± 0.76

 a M_{d30} = temperature at which 50% of martensite is formed in tension after a true strain of 0.30 [calculated Ref. (3)]. b M_s = martensite starting temperature.

defectiveness, phase transitions, is undoubtedly important from a basic standpoint as well.

For each material in every state of cold work the main aspects of the electrochemical and corrosion behavior are delineated by the corrosion rates *vs.* time curves (determined, for example, by the Stern-Geary method), by the polarization curves of anodic dissolution and cathodic hydrogen evolution, and by the passivation and passivity parameters. Each state of cold work is characterized by the type of the deformation process and by the rate, temperature and degree of the deformation itself. The effect of the orientation of the specimen surface under study with respect to the deformation direction must be taken into account as



Fig. 3. Cathodic polarization curves for hydrogen evolution on AISI 316 L steel in deaerated 1M H_2SO_4 solution at 25°C for different values of the deformation degree (indicated as a percentage). Deformation by rolling at both rcom and liquid N_2 temperature; long transversal (T_L) section. Potential values are relative to SSE.

well. The development lines of our research and the principal results successively obtained are explained below (1).

Regarding the phenomenological aspects of the electrochemical and corrosion behavior in deaerated sulfuric acid solution of the austenitic stainless steels AISI 304 L, 304, and 316 deformed by application of a tensile stress (AISI 304 L steel was deformed also by cold drawing), the following points came to light.

(i) The cold working of the material leads to an increase in the generalized and uniform corrosion rate in the active region. This influence was observed on the surfaces orientated perpendicularly or at 45° to the deformation direction, above a critical threshold of the deformation degree of roughly 15% for all the steels studied. The susceptibility to the effect of the



Fig. 4. Potentiodynamic (30 mV/min) anodic polarization curves of AISI 304 L steel in deaerated 1M H_2SO_4 solution at 25°C for different values of the deformation degree (indicated as a percentage). Deformation by rolling at both room and liquid N_2 temperature; long transversal (T_L) section. Potential values are relative to SSE.

cold working increases in the sequence AISI 316 < AISI 304 < AISI 304 L.

(ii) A decrease in the overvoltage of the cathodic hydrogen evolution always corresponds to an increase



Fig. 5. Potentiodynamic (25 mV/min) anodic polarization curves of AISI 304 L steel in deaerated 0.1M HCl solution at 25°C for different values of the deformation degree (indicated as a percentage). Deformation by tension at both room and liquid N_2 temperature; transversal (T) section. Potential values are relative to SSE.



Fig. 6. Potentiodynamic (25 mV/min) anodic polarization curves of AISI 304 L steel in deaerated 0.1M HCl solution at 25°C for different values of the deformation degree (indicated as a percentage). Deformation by tension at both room and liquid N_2 temperature; longitudinal (L) section. Potential values are relative to SSE.



Fig. 7. Critical pitting potential of AISI 316 L steel in the artificial physiological solution of the composition given below, as a function of the deformation degree and the orientation of the exposed surface to the deformation direction, for the different types of cold working (at room temperature). Solution of 8.74 g/liter NaCl, 0.35 g/liter NaHCO₃, 0.06 g/liter Na₂HPO₄, 0.06 g/liter NaH₂PO₄, pH 7, in atmosphere of N₂ gas, at 38°C. L, T, T_s, and T_L correspond to longitudinal, transversal, short or long transversal sections, respectively. Potential values are relative to SSE.

in the corrosion rate with the deformation degree, whereas the anodic behavior in the active region of the considered materials is not appreciably affected.

(*iii*) Extending the investigation beyond the active region, a larger work hardening of the material results in an unfavorable effect, which is enhanced by the addition of chlorides, on the formation of the passivating films and sometimes on their protective characteristics as well. The surfaces parallel to the deformation direction generally exhibit a more stable passivity.

Regarding the structural effect of the cold plastic deformation, i.e., texture, surface defectiveness, phase transitions, to which the decreases in the hydrogen overvoltage (and the corresponding increases in the corrosion rate) can be ascribed, the following points may be underlined.

(i) In the case of deformation by application of a tensile stress, the preferred orientation of the crystal grains is negligible. On the other hand, the drawn steel AISI 304 L assumes a certain degree of fibrous texture in the [111] direction. The measurements performed in our Institute on the various faces of single crystals of



Fig. 8. Critical pitting potential of AISI 316 L steel in the artificial physiological solution of the composition given in Fig. 7 as a function of the deformation degree and the orientation of the exposed surface to the deformation direction. Deformation by tension at both room and liquid N_2 temperature. Potential values are relative to SSE.



Fig. 9. Critical pitting potential of AISI 304 L steel in the artificial physiological solution of the composition given in Fig. 7 as a function of the deformation degree and the orientation of the exposed surface to the deformation direction. Deformation by tension at both room and liquid N_2 temperature. Potential values are relative to SSE.

austenitic stainless alloy have shown, moreover, that the highest hydrogen overvoltage values correspond exactly to this direction (2).

The cold plastic deformation which, as already seen, causes the hydrogen overvoltage to decrease must therefore act through the other structural effects (that is, through the increase in structural defects emerging on the specimen surface and/or the occurrence of phase transitions).

(ii) The density of the structural defects does not increase progressively with the deformation degree, but shows a steep rise for a deformation value of about 15%. Above this value, the density of the observed deformation bands increases according to the sequence AISI 316 < AISI 304 L < AISI 304. It was found that these bands are also composed of deformation twins, while in the case of the strongly deformed steel 304 L the presence of α' -martensite generated by the phase

transformation of austenite to martensite as a consequence of the deformation itself was detected.

The inversion noted between the AISI 304 and AISI 304 L in the relationship between the "structure" (density of the deformation bands higher in the AISI 304) and the electrochemical and corrosion behavior (susceptibility to the effect of cold plastic deformation higher for AISI 304 L) must, in our opinion, be ascribed to the presence of α '-martensite in the AISI 304 L. The research subsequently developed toward isolating the effect exerted on the electrochemical and corrosion behavior of the AISI 304 L and 316 L steels by the phase transformation of austenite to martensite from the one due to the presence of defects.

The choice of these steels was determined not only by their intrinsic structural instability which makes them particularly suitable for the purpose, but also by their importance in technologically advanced fields. In particular, the AISI 316 L is practically insusceptible to intergranular corrosion and is resistant to pitting; its behavior in the work-hardened state is especially interesting in view of its application as a material for surgical plants in the human body.

Experimental

In order to separate and compare the effect of both the martensite and that due to the defects, cold plastic deformation of the AISI 304 L and 316 L steels² was carried out by either tension, drawing, or rolling at room temperature as well as at liquid nitrogen temperature (-196° C) so as to obtain significant amounts of martensite.

Details of the material working schedule (solution heat-treatment, deformation,³ cutting, surface preparation), of the microstructural analysis, and of the electrochemical experimental techniques, polarization cell, and electrode assembly have already been described elsewhere (1, 4).

Cathodic polarization curves relative to the hydrogen evolution on the considered steels were recorded

² Chemical compositions and some structure characteristics of the considered steels are given in Table I. ³ Reductions in the cross-sectional area were always adopted to express the deformation degree.



Fig. 10. Vickers hardness of AISI 304 L and 316 L steels as a function of the deformation degree and the orientation of the specimen surface to the deformation direction. Deformation by rolling at both room and liquid N_2 temperature.





Fig. 11. Deformation twins in AISI 316 L steel deformed 15% by tensile stress at room temperature: (a) bright-field image; (b) electron diffraction pattern, $[\bar{1}01]_{\gamma}$ zone axis; (c) dark-field image obtained by 020 γ -twin reflection.

in a 1M H_2SO_4 solution, deaerated and stirred by circulation of N_2 gas, at a temperature of 25°C. Anodic polarization curves were recorded in both a 1M H_2SO_4 and a 0.1M HCl (5) solution in an atmosphere of N_2 gas at 25°C.

Critical pitting potentials of the considered steels⁴ were determined in an artificial "physiological" solu-

 $^4\,A$ passivation pretreatment was carried out by dipping the specimens in 30% HNOs solution at 55°C for 30 min.

Fig. 12. e-hexagonal martensite bands in AISI 304 L steel deformed 15% by tensile stress at room temperature: (a) bright-field image; (b) electron diffraction pattern, $[0\bar{1}1]_{\gamma}$ and $[10\bar{1}\bar{1}]_{\epsilon}$ zone axes; (c) dark-field image obtained by $10\bar{1}1$ ϵ -reflection.

tion, simulating the aggressiveness of the human body, of the following composition: 8.74 g/liter NaCl, 0.35 g/liter NaHcO₃, 0.06 g/liter Na₂HPO₄, 0.06 g/liter NaH₂PO₄, pH 7, in atmosphere of N₂ gas, at 38° C (4). These measurements were performed by applying the "scratching" technique introduced by Pessall and Liu (6). The electrode potential was maintained constant with the potentiostat at a selected value below the ex-



Fig. 13. α' -cubic martensite plates in deformation twins in AISI 304 L steel deformed 15% by tensile stress at room temperature: (a) bright-field image; (b) electron diffraction pattern, [111] γ and [411] γ -twin zone axes; (c) dark-field image obtained by 131 γ -twin reflection; (d) dark-field image obtained by 112 α' -reflection.

pected pitting potential and then the specimen surface was scratched with a tungsten point (Fig. 1). The current/time relationship was recorded for a few minutes until the specimen repassivated. This procedure was continued with the electrode potential adjusted by 25 mV steps to more and more noble values, until the scratch failed to repassivate, a failure which was indicated by a gradual current rise in time; the presence of pits developed at the scratched site was verified microscopically. The electrode potentials were always referred to the Hg, Hg_2SO_4/K_2SO_4 (saturated) electrode (SSE) whose potential relative to the standard hydrogen electrode at 25°C is +642 mV.

Results and Discussion

Some results of the electrochemical measurements are given in Fig. 2 to 9. The lowering effect on the hydrogen overvoltage produced by increasing the deformation degree is higher when the cold working of the considered steels is carried out at the liquid nitrogen temperature; at room temperature the influence of the cold plastic deformation is much more notable for the AISI 304 L than for the AISI 316 L steel (Fig. 2 and 3).

On the anodic side, the change from sulfuric acid (Fig. 4) to hydrochloric acid (Fig. 5 and 6) solution magnifies the unfavorable effects of the degree of work hardening on the occurrence of the passivation phenomena and on the protective characteristics of the passivating films to an extent which depends on the orientation of the specimen surface with respect to the deformation direction and on the temperature at which the cold plastic deformation is carried out. All the types of cold plastic deformation—by either tension, drawing, or rolling—cause the critical pitting potential of the considered steels to diminish as shown in Fig. 7-9. Again, a considerable anisotropy of this property was observed; for example, for the rolling the critical pitting potential decreases, the degree of work hardening remaining unchanged, from the longitudinal (L) section to the short transversal (T_s) one and from the latter to the long transversal (T_L) section. An influence of the cold working temperature again came to light (Fig. 8). For the AISI 304 L steel (Fig. 9) the susceptibility to the pitting corrosion is greater (as is well known), but it appears to be less affected by the deformation degree than for the AISI 316 L steel.

The relationship between the previously described aspects of the electrochemical behavior of the considered steels and the structural effects of the cold plastic deformation would need a complete, systematic, and quantitative study of these latter, whereas only some qualitative "flashes" will be shown here. All the same, we think they are already sufficiently meaningful.

First of all, a general idea of the work-hardening effects of the materials is given by the Vickers hardness diagrams of the type in Fig. 10, which, at least in the case of cold rolling at the liquid nitrogen temperature, exhibits an anisotropy of this property.

Investigations by transmission electron microscopy, electron diffraction, and x-ray diffraction enabled us to get a qualitative picture of the structure of the AISI 304 L and 316 L steels deformed by tension at both room and liquid nitrogen temperature. This picture includes dislocations density, presence and nature of the deformation bands [*i.e.*, deformation twins (Fig.

Table II. Results of the observation under the electron microscope of AISI 304 L and 316 L steels deformed by tensile stress

Austenitic	Deformat	ion	Dislo- cations	Deformation	Bands	nature			
steel	Temperature	(%)	(cm/cm ^s)	bands	Twins	tensite	α' -martensite	Austenite	
AISI 304 L	Room temper-	0	1.3 × 10°	No	No	No	No	~100%	
	ature	10	$\simeq 1.5 \times 10^{10}$	Few	Yes	Not ob- served	No	≃100%	
		15 30	$>2 \times 10^{10}$ >2 × 10^{10}	Medium quantity Many	Yes	Yes	Little	Largely prevail- ing	
	Liquid N ₂ tem-	9		Many	Yes	Not ob- served	Medium amount	Prevailing	
	perature	13		Largely prevailing	Yes	Not ob-	Much	Much	
		19	-	Scarcely discernible			Very much	Little	
AISI 316 L	Room temper- ature	0 10	$1.17 \times 10^{9} \simeq 1 \times 10^{10}$	No Probably not pres-	-	-	Largely prevail- ing	Not observed	
		15	$\simeq 2 \times 10^{10}$	ent Few	No No	No No	No No	100% 100%	
		30	>2 × 1010	Medium quantity	Yes	Not ob- served	No	~100%	
	Liquid N ₂ tem- perature	9		Many	Yes	Not ob- served	Not observed	Largely prevail-	
	•	13 19	Ξ	Prevailing Yet discernible	Not ob- served	Yes	Medium amount	Prevailing	
							Much	Medium amount	
							Prevailing	Little	

Table III. Qualitative results of the x-ray diffraction measurements for AISI 304 L and 316 L steels deformed by tensile stress

Deformation			AISI 304 L		AISI 316 L			
Temperature	(%)	(111)γ	(110) <i>a'</i>	(1011).	(111)γ	(110) <i>a'</i>	(1011),	
Poor tompor	10	ş	VW		s			
ature	30 9	S	W W W ÷ M	vw	5 5 5	- w		
Liquid N ₂ tem- perature	13 19	M W	$\mathbf{M} \stackrel{\mathbf{M}}{\div} \mathbf{S}$	VW VW	M ÷ S M	W M	vŵ vw	

S = strong; M = medium; W = weak; VW = very weak.

11), ϵ -hexagonal martensite (Fig. 12), or slip bands which cannot be morphologically distinguished from each other], presence of α' -cubic martensite (Fig. 13), and residual austenite. The results are summarized in Tables II and III.

In the case of deformation at room temperature, the behavior of the considered steels is quite different; the dislocations density as well as the density of the deformation bands is always higher in the AISI 304 L than in the 316 L steel. Moreover, in the strongly deformed 304 L steel, α' -martensite is present in amounts increasing with the deformation degree, whereas the 316 L steel does not exhibit any phase transition even in the state of maximum deformation (in accordance with the M_{d30} values given in Table I).

In the case of deformation at the liquid nitrogen temperature, the behavior of the considered steels becomes essentially the same for both of them in that the phase transition of austenite to martensite is always notable or even prevailing; nevertheless a greater structural instability of the AISI 304 L steel compared with the 316 L is confirmed.

Much more research work must be carried out on the structural aspects, also as regards the spatial distribution and orientation of the formed martensite and the influence on the passivating films, in order to explain

the previously described anisotropy effects on the electrochemical behavior of the deformed steels.

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REFERENCES

- W. Nicodemi, P. Pedeferri, and D. Sinigaglia, Met. Ital., 63, 23 (1971); D. Sinigaglia, P. Pedeferri, B. Mazza, G. P. Galliani, and L. Lazzari, ibid., 65, 77 (1973); B. Mazza, P. Pedeferri, D. Sinigaglia, U. Della Sala, and L. Lazzari, Werkstoffe Korro-cian, 25 220 (1974) sion, 25, 239 (1974).
- 2. A. La Većchia, L. Péraldo Bicelli, and C. Romagnani, Ann. Chim., **62**, 489 (1972). 3. T. Angel, J. Iron Steel Inst., **168**, 165 (1954); F. C.
- Hull, Welding J. (Res. Suppl.), 52, 1938 (1973). 4. A. Cigada and P. Pedeferri, Ann. Chim., 65, 509
- (1975). 5. M. Da Cunha et al., Mem. Sci. Rev. Met., 70, 725 (1973)
- 6. N. Pessall and C. Liu, Electrochim. Acta, 16, 1987 (1971).