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Influence of Cold Plastic Deformation on Critical Pitting Potential of AISI 316 L and 304 L Steels in an Artificial Physiological Solution Simulating the Aggressiveness of the Human Body

A. CIGADA, B. MAZZA, P. PEDEFERRI, and D. SINIGAGLIA,
Istituto di Chimica-fisica, Elettrochimica e Metallurgia del Politecnico di Milano, Centro di Studio del C.N.R. sui Processi elettrodici, 20133 Milano, Italy

Summary

The effect of cold working on critical pitting potential of AISI 316 L and 304 L steels in a buffered physiological solution has been studied. In particular, the importance of deformation degree, orientation of the specimen surface to the deformation direction, and cold working temperature in lowering the critical pitting potential is shown.

Several observations have been reported on the unfavorable effects of the cold working on the corrosion resistance of the AISI 316 L steel in the human body or in artificial solutions simulating its aggressiveness; however, systematic studies are missing.

Our research work carried out on different austenitic stainless steels in different aggressive media[1,2] led us to establish that the worsening of the corrosion behavior of these materials in the work-hardened state generally depends on the following factors: 1) the composition of the aggressive medium, the presence of chloride ions being especially harmful; 2) the type of steel; 3) the deformation degree, the type of cold working (e.g., by tension, drawing or rolling), and the conditions of the deformation process (e.g., rate, temperature, etc.); and 4) the orientation of the specimen surface under study with respect to the deformation direction.

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This paper shows the results of the study concerning the aptitude to local repassivation of the work-hardened AISI 316 L steel in a buffered physiological solution simulating the aggressiveness of the human body. This aptitude has been characterized in terms of critical pitting potential determined by the "scratching" technique introduced by Pessall and Liu[3], i.e., the potential above which a scratch in the surface passivating film fails to cicatrize.

As has been pointed out in literature, the Pessal and Liu technique is a valid approach for the determination of the pitting susceptibility of a metallic material in a certain environment in view of the solution of practical problems such as the ones manifested in surgical plants in the human body, where there is the need to know whether or not a real structure will pit under given conditions.

For the sake of comparison, the AISI 304 L steel has also been studied.

In order to attain a deeper knowledge of the influence of the structural modifications induced by the deformation (in general, texture, surface defectiveness, phase transitions), the cold working has been carried out not only at room temperature but also at liquid nitrogen temperature, so as to obtain significant amounts of martensite generated by the phase transformation of austenite.

PROCEDURE

Chemical compositions of the stainless steels studied are given in Table I.

Details of the material working schedule (solution heat-treatment, cold working, cutting, surface preparation including passivation treatment) of the structural analysis and of the measurement cell and electrode assembly have been largely described elsewhere.[1,2,4]

The experimental procedure can be summarized as follows. The first step was the solubilization of any carbides present by heating to 1050°C for 1 hr with subsequent cooling in water; next was the deformation of the test pieces kept at room temperature or at liquid nitrogen temperature (-196°C) by either tension, drawing, or rolling. (The values of the reduction in area of the cross sections of the test pieces and the main characteristics of the deformation processes are given in Table II.) The specimens were then cut to obtain the different surface orientations with respect to the deforma-

TABLE I

Chemical Composition of the Stainless Steels Studied

Austenitic Stainless Steel	Type of Cold Working	Composition (wt %)								
		C	Si	Mn	P	S	Cr	Ni	Mo	N
AISI 316 L	Tension	0.022	0.43	1.51	0.033	0.023	16.80	10.65	2.90	0.033
	Drawing	0.023	0.40	1.45	0.034	0.021	16.60	10.90	3.00	0.037
	Rolling	0.026	0.41	1.24	0.008	0.011	16.10	10.90	2.20	0.034
AISI 304 L	Tension	0.025	0.45	1.39	0.023	0.021	18.60	8.75	0.50	0.036
	Drawing	0.027	0.47	1.39	0.035	0.021	18.60	8.75	0.50	0.037
	Rolling	0.020	0.41	1.40	0.032	0.013	18.10	10.30	0.32	0.039

TABLE II

Main Characteristics of the Deformation Processes and Reductions in the Cross-Sectional Area

		Deformation	
Type	Temperature	Rate (as indicated in the different cases)	Degree (reduction in the cross-sectional area) (%)
Tension	Room temperature	$0.05\ kg/mm^2 \cdot sec$ (rate of increase in the applied stress)	10 15 30
	Liquid nitrogen temperature	$0.13\ kg/mm^2 \cdot sec$ (Idem)	9 13 19
Drawing	Room temperature	1.5 mm/sec (rate of advancement of the draw head)	10 30 50
	Liquid nitrogen temperature	5 ÷ 10 mm/sec (Idem)	10 30 50
Rolling	Room temperature	4 m/min (speed of the unloaded rolls)	10 30 50
	Liquid nitrogen temperature	4 m/min (Idem)	10 30 50

tion direction [i.e., parallel or longitudinal (L) surfaces and perpendicular or transversal (T) surfaces in the cases of tension and drawing; longitudinal (L), long-transversal (T_L) and short-transversal (T_S) surfaces in the case of rolling].

Surface preparation of the specimens was accomplished by the following operations: wet polishing on emery papers with decreasing grain size up to 20 μm; electropolishing in a solution of ethanol and perchloric acid; polishing with diamond pastes with decreasing grain size up to 1 μm; rinsing in denatured alcohol and then in distilled water in the presence of ultrasounds; passivation in a solution of nitric acid (concentration, 30%; temperature, 55°C; duration, 30 min); rinsing in distilled water.

Critical pitting potentials (E_c) of the considered steels were determined in an artificial "physiological" solution, simulating the aggressiveness of the human body, of the following composition: 8.74 g/l. NaCl, 0.35 g/l. $NaHCO_3$, 0.06 g/l. Na_2HPO_4, 0.06 g/l. NaH_2PO_4; pH 7, in an atmosphere of N_2 gas, at 38°C. These measurements were performed by applying the following procedure.[3] The electrode potential was maintained constant with the potentiostat at a selected value below the expected pitting potential; then the specimen surface was scratched with a tungsten point. The current–time relationship was recorded for a few minutes until the scratch 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; this failure was indicated by a gradual current rise in time. The presence of pits developed at the scratched site was verified microscopically.

Measurements were reproducible within the limits of 25 mV (50 mV at the most). Electrode potentials were always referred to the Hg, Hg_2SO_4/K_2SO_4 (sat.) electrode (= SSE), whose potential relative to the standard hydrogen electrode at 25°C is +642 mV.

Reductions in the cross-sectional area were always adopted to express the deformation degree. A general idea of the work-hardening effects of the materials is given by the results of the Vickers hardness tests (Fig. 1). Vickers hardness number (VHN) increases with the deformation degree as a result of the increased defectiveness and especially of the induced phase transformation of austenite in harder structures (ϵ- and α'-martensite). The anisotropy of this property, at least in the case of cold working at the liquid nitrogen temperature, must be mentioned.

RESULTS

For all types of cold working (by either tension, drawing, or rolling), a decrease in the critical pitting potential with the deformation degree is generally observed (Figs. 2–4). Moreover, a strong anisotropy of the behavior of specimen surfaces with different orientations to the deformation direction must be emphasized. This ani-

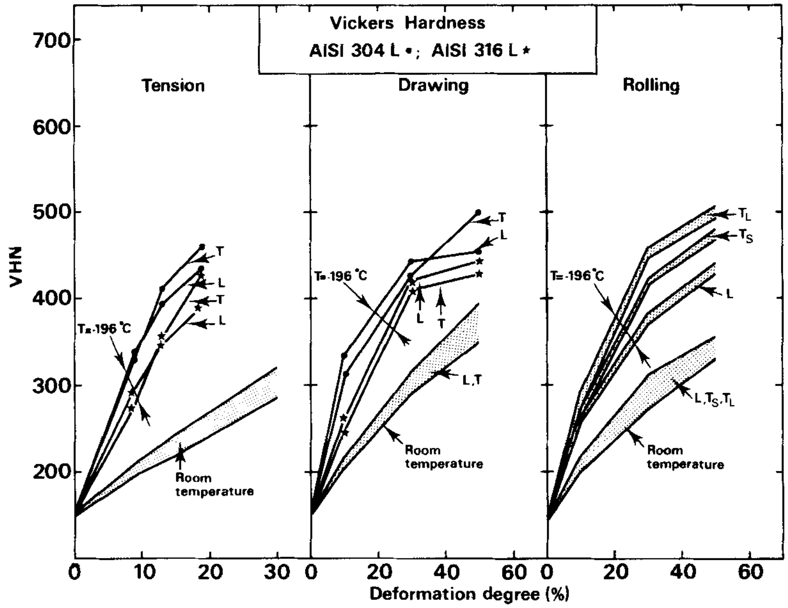

Fig. 1. Vickers hardness number (VHN) of AISI 316 L and 304 L steels as a function of the following factors: deformation degree, orientation of the specimen surface to the deformation direction, type and temperature of deformation.

sotropy is enhanced by increasing the deformation degree, but it is manifested even in a material not deformed by cold working. Obviously, this can be explained only by the influence of the operations undergone by the test pieces independently of cold working (i.e., hot-drawing and hot-rolling), an influence that is not canceled out by the solubilization treatment.

In any event, the critical pitting potential of the AISI 316 L steel decreases, the deformation degree remaining unchanged, from the longitudinal section to the transversal one, in the cases of deformation by tension and drawing, and from the longitudinal section to the short-transversal one, and from the latter to the long-transversal section for the rolling.

This behavior of the 316 L steel is not changed qualitatively by varying the deformation temperature (i.e., room temperature or liquid nitrogen temperature), except that more positive (noble)

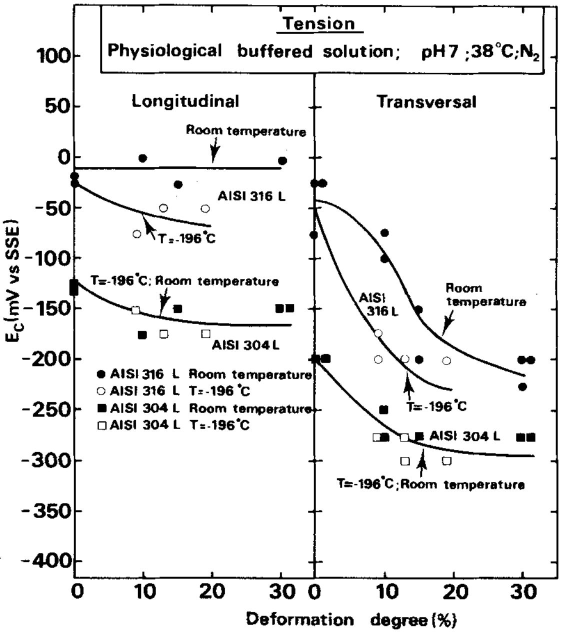

Fig. 2. Critical pitting potential E_c of AISI 316 L and 304 L steels in an artificial physiological solution (see text for the composition) as a function of the following factors: deformation degree, orientation on the specimen surface to the deformation direction, and deformation temperature. Deformation by application of tensile stress. Potential values are relative to a saturated mercury sulfate electrode, SSE.

values of the critical pitting potential are generally found after cold working at liquid nitrogen temperature. In particular, for the rolling at liquid nitrogen temperature, a smaller decrease in the critical pitting potential on the short-transversal, and especially on the long-transversal surfaces, is observed (e.g., a maximum decrease of $\simeq$100 mV by passing from the longitudinal section to the long-transversal one, in comparison with the corresponding decrease of $\simeq$250 mV for the rolling at room temperature).

As far as the influence of the deformation type (i.e., by tension, drawing, or rolling) is concerned, it appears to be negligible, the small differences being due to the different steel compositions (but all referable to the AISI 316 L type, Table I).

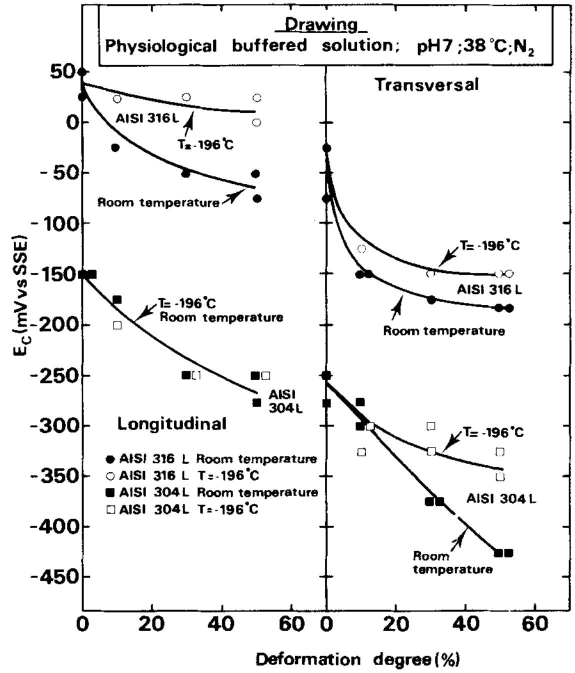

Fig. 3. Critical pitting potential E_c of AISI 316 L and 304 L steels, in the same artificial physiological solution as in Fig. 2, as a function of the following factors: deformation degree, orientation of the specimen surface to the deformation direction, and deformation temperature. Deformation by drawing. Potential values are relative to a saturated mercury sulfate electrode, SSE.

For the AISI 304 L steel, as is well known, the resistance to the pitting corrosion is lower, i.e., the critical pitting potentials are less noble than for the 316 L steel, both in the state of not deformed material and in the work-hardened state.

Nevertheless, under certain conditions, the critical pitting potential of the 304 L steel is less affected by the deformation degree, so that this steel may become similar in behavior to the 316 L one at the highest values of the deformation degree (e.g., in Fig. 4, for the rolling at room temperature, the case of long-transversal section). Moreover, it must be pointed out that in the case of the cold-rolled 304 L steel, the critical pitting potential for the different orientations of the exposed surface decreases in the sequence $L > T_L > T_S$ at

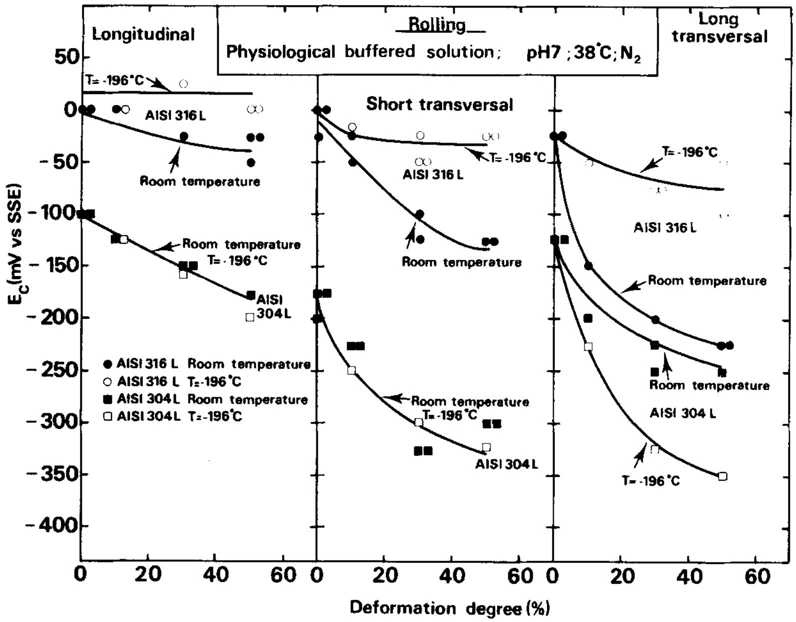

Fig. 4. Critical pitting potential E_c of AISI 316 L and 304 L steels, in the same artificial physiological solution as in Fig. 2, as a function of the following factors: deformation degree, orientation of the specimen surface to the deformation direction, and deformation temperature. Deformation by rolling. Potential values are relative to a saturated mercury sulfate electrode, SSE.

room temperature, or $L > T_L \simeq T_S$ at liquid nitrogen temperature; however, in the case of the cold-rolled 316 L steel, the sequence is always $L > T_S > T_L$.

CONCLUSIONS

Cold plastic deformation causes the resistance to the pitting corrosion of the AISI 316 L and 304 L steels to diminish with considerable anisotropy effects in relation to the different orientation of the exposed surface with respect to the deformation direction. This result accounts for worse behavior, as far as the aptitude to local repassivation and susceptibility to pitting are concerned, of those surfaces which are perpendicular to the main surfaces exposed to an aggressive environment (e.g., referring to surgical plants in the human body, the internal surfaces of through holes in cold-rolled plates, apart from the crevice corrosion phenomena that usually arise in these conditions).

For applications in surgical plants in the human body, the cold-rolling of AISI 316 L steel plates at liquid nitrogen temperature, on the one hand, would further improve the mechanical resistance; on the other hand, it would not worsen the susceptibility to pitting and the aptitude to local repassivation in such a great measure as in the case of cold-rolling at room temperature (e.g., apart from crevice corrosion phenomena, accidental scratches in the passivating films would cicatrize more easily even on the weakest surfaces such as the short-transversal and long-transversal ones).

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