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Electrochemical and corrosion behaviour of cold rolled AISI 301 in 1 M H_2SO_4

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Abstract

Stainless steels (SS) are widely used in several fields. In recent years, the good corrosion resistance as well as the remarkable mechanical properties of SS have made it an even more utilised material. Such extensive utilisation produces new concern about its ability to maintain good properties after many working processes. In this paper an AISI 301 SS with different degrees of cold deformation has been considered. The cold working of these materials produces some important changes in the microstructure (i.e. grain size, crystallographic texture) and involves phase transformations ($\gamma \rightarrow \alpha'$). Electrochemical measurements have been used to investigate the corrosion behaviour of the alloy in sulphuric acid in the presence of chlorides. In the anodic behaviour of the cold rolled with respect to the annealed SS, a moderate variation of the passivity region but a remarkable increase of the current density was observed. Morphological analyses have been performed to relate the electrochemical results to the alloy structure. The relationship between metallurgical properties and corrosion behaviour has been discussed.

Keywords: Stainless steel; Corrosion; Work hardening; Cold rolling

1. Introduction

There has been a significant increase in the use of stainless steel in chemical plants, transport, the household electrical industry, etc. Such wide applications are due to its high mechanical workability, resistance to high and low temperatures and corrosion resistance. The possibility of cold working these materials, specially the austenitic stainless steels, is exploited in many applications. Moreover such an operation produces a hardening process which remarkably improves the mechanical properties. Especially the AISI 301 steel, which is characterised by a metastable structure [1], develops yielding strength of 300 MPa in normal conditions, which is expected to reach 1500 MPa when strongly deformed [2]. Such modification of the mechanical properties is mainly due to the partial transformation of austenite to martensite ($\gamma \rightarrow \alpha'$) and by the extra dislocation introduced by strain. This effect is an essential requisite for structural parts where resistance and torsional rigidity are necessary.

Cold rolling is an important production process for stainless steel; it starts from hot rolled coils some millimetres thick, proceeds with steps of cold deformation and finishes reaching thicknesses of some tenths of a millimetre. Annealing follows each step of cold rolling, where the thickness reduction does not exceed 70%. The resulting tension distribution of the cold rolled strips is finally homogenised by a tension leveller. The SS 301 is suitable for these processes, allowing a controlled modulation of the mechanical resistance. On the other hand corrosion properties could be modified in an uncontrolled way [3–5].

This paper deals with the modification of AISI 301 when subjected to different degrees of deformation by cold rolling and its effect on the corrosion resistance in sulphuric acid solution containing chlorides.

2. Experimental details

2.1. Materials

The starting material was 3-mm thick hot rolled AISI 301 stainless steel having the following composition (wt%) 0.12 C, 17.13 Cr, 6.69 Ni, 1.02 Mn, 0.65 Si, 0.04 N. After several cold rolling steps, the final thickness ranged between 0.4 and 0.7 mm. The annealing performed at the end of each deformation step was carried out in pure hydrogen at 1130°C. The time to reach this temperature in

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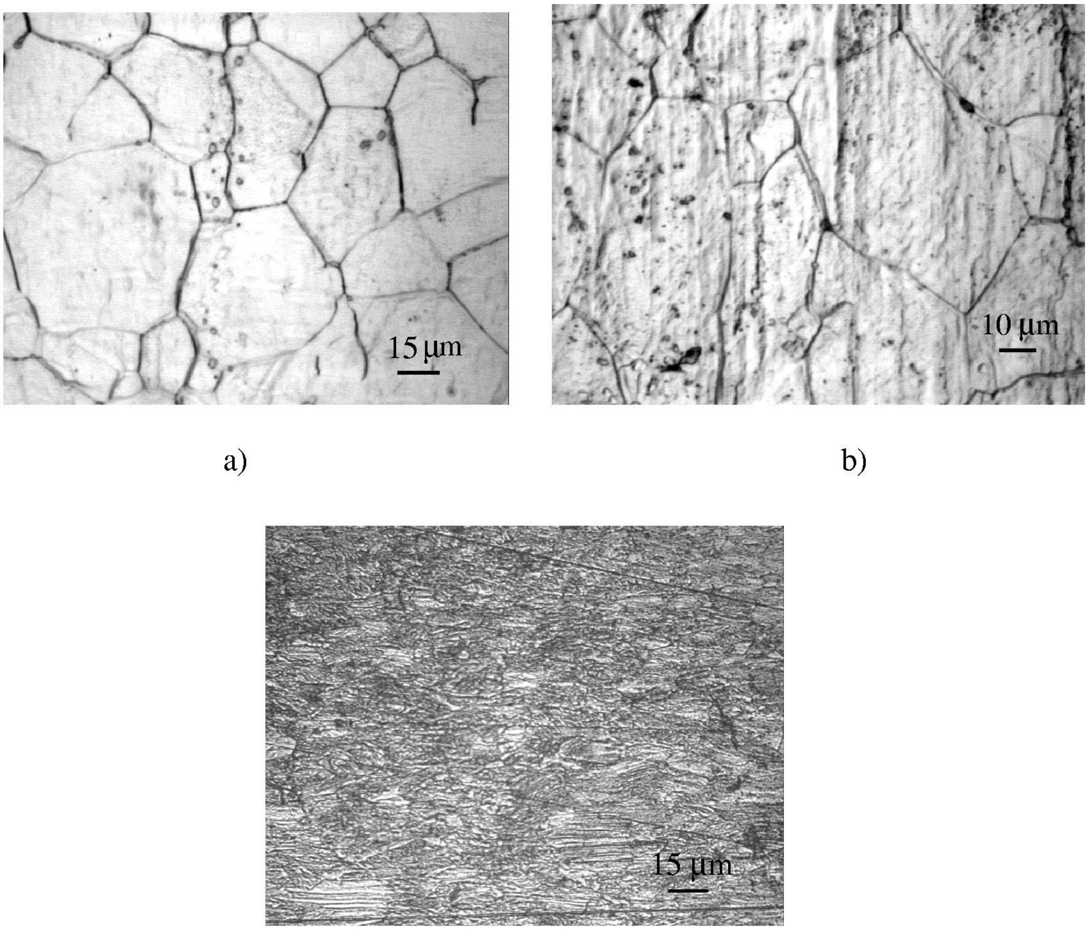
Table 1
Degree of cold deformation and mechanical parameters of the studied alloys

Sample	Reduction[a] %	Tensile strength (MPa)	0.2% Yielding strength (MPa)	$\epsilon_{50\%}$[b]	HV (2 kg)
1 (annealed)	–	804	381	48	223
2	27	1207	980	21.8	365
3	45	1403	1343	7.37	455
4	60	1655	1507	2.82	496

[a] Thickness reduction in the last cold rolling step.
[b] Strain percentage at 50% of the maximum stress.

the furnace depends on the thickness of the coil and it is determined according to a standard procedure used in industrial plant. However, the heating time plus the time at 1130°C ranges from 40 to 80 s in the samples studied. The cooling is obtained by injection of pure hydrogen and the time required to reach room temperature ranges between 40 and 90 s. For samples 2, 3 and 4 the last deformation, which determines the degree of cold deformation, is not followed by any thermal treatment. The thickness reduction related to the last cold rolling pass and the respective mechanical properties are reported in Table 1.

The thickness reduction during the process determines the degree of work hardening. Such mechanical deformation induces important changes in the alloy structure, grain elongation and phase transformation ($\gamma \rightarrow \alpha'$). The transition from austenite (γ) to martensite (α') has been detected by Ròmio et al. [6] on these materials by X-ray diffraction technique with a Mo kα radiation in the θ window 9–24°.



a)

b)

c)

Fig. 1. (a) Austenitic equiaxed grain structure for the annealed sample; small islands of ferrite were detected; (b) austenitic structure with presence of precipitates in sample 2; (c) martensite formation in heavily deformed austenite grains in the most work hardened sample.

Such phase transformation produces an amount of α' phase that depends on the degree of work hardening: 35% for sample 2, 58% for sample 3 and 84% for sample 4. Moreover, the amount of phase transformation varies from the surface to the bulk of the sheet, for instance, in the most work hardened sample the amount of α' measured on the surface and at a 0.1 mm below the surface is equal to 84 and 63%, respectively. The same authors [6] detected, by TEM, a large number of dislocations casually oriented in the most work hardened samples and small dislocation density and twins characteristic of austenite in the annealed sample. Moreover, the SS texture analysed by the direct polar figures obtained from X-ray diffraction, pointed out that the cold rolling produces a dominant orientation of the {110} plane of the crystallites parallel to the rolling plane, typical of laminated foils having cubic structure and low stacking fault energy like SS, with a ⟨112⟩ direction parallel to the rolling direction. The annealing of the cold rolled SS determines a partial redistribution of the crystallites along the direction {100}⟨001⟩.

In Fig. 1 the structures of the annealed (sample 1) and the deformed materials (sample 2 and 4) are presented. These picture highlight how the equiaxed structure of the annealed sample under the moderate cold deformation produces precipitates in the grain boundaries and finally an extensive formation of martensite.

2.2. Electrochemical measurements

The samples were embedded in epoxy resin and mechanically polished with diamond paste (up to 1-μm grade). The surface area exposed to the test solution was 3 mm^2. Electrochemical experiments (potentiodynamic and chronoamperometric measurements) were performed using a remote controlled potentiostat/galvanostat (273A, EG&G Princeton Research) with dedicated software (M342, EG&G Princeton Research). A three-compartment cell was used. The potentiodynamic measurements were run when the electrode potential reached a steady state and the potential sweep-rate was fixed at 0.5 mV/s. The test solution was aerated 1 M sulphuric acid aqueous solution. Different amounts of chlorides were also added to the test solution. Only transversal sections with respect to the lamination direction were analysed, because of the different residual stresses that can be present in the cold rolled steel strip.

3. Results and discussion

The typical potentiodynamic result obtained in the studied systems during the electrochemical investigation shows a wide passivity range characterised by a low passivity current (Fig. 2).

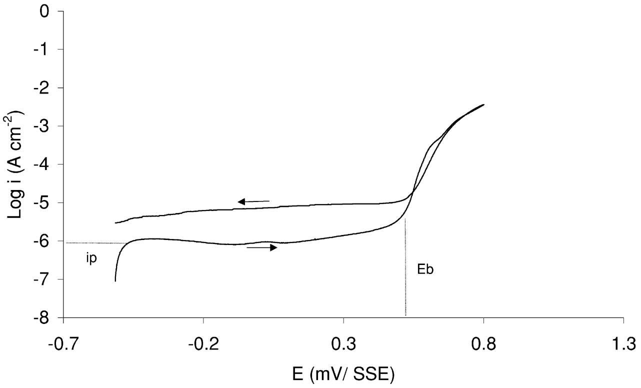


Fig. 2. Anodic polarisation of sample 3 in 1 M H_2SO_4+10 000 ppm of Cl^-.

The passivity breakdown potential, E_b, was evaluated by performing chronoamperometric measurements at different potentials in the range of the passivity breakdown singled out with the potentiodynamic experiments. Fig. 3a shows that E_b did not display any dependence on the degree of work hardening.

The trend of the passivity current values, i_p, is reported in Fig. 3b. The diagram shows how the free chloride sulphuric acid solution allows a perfect passivation of the stainless steel, independently from the degree of work hardening. As the chloride content rises, the greater the work hardening, the weaker the passivity layer. The increase of the passive current density was already observed in austenitic SS of 304 type and was ascribed to the higher critical current for passivation of martensite formed during cold work [7]. Considering sample 2 (27% of thickness reduction) it is worth noticing that the increase of current density in the passivity range is negligible, even if precipitates (Fig. 1b) and a remarkable formation of martensite have been detected. However, the $\epsilon_{50\%}$ value equal to 21%, quite high at this deformation level, is characteristic of a material which owns a good plasticity, i.e. is able to relax internal stresses induced by martensite formation.

Fig. 4 shows the dependence of some important parameters ($\epsilon_{50\%}$, martensite content, HV and i_p) with the thickness reduction of the rolled foils and highlights that there is not a direct relationship between martensite formation and passivity current increase. Moreover, this phase transformation could hardly be separated from the other possible causes of the anticorrosive property decay of SS (crystallographic texture, dislocation density, internal stresses . . .). Other papers [8–10] describe the detrimental effect of cold working on corrosion resistance, mainly on 304 and 316 SS, but they do not determine the contribution of the different SS modifications in their final anticorrosive decay. The possibility to change the amount of strain-induced martensite formed during cold working depending on the number of rolling passes and the rolling rate, maintaining constant thickness reduction and SS com-

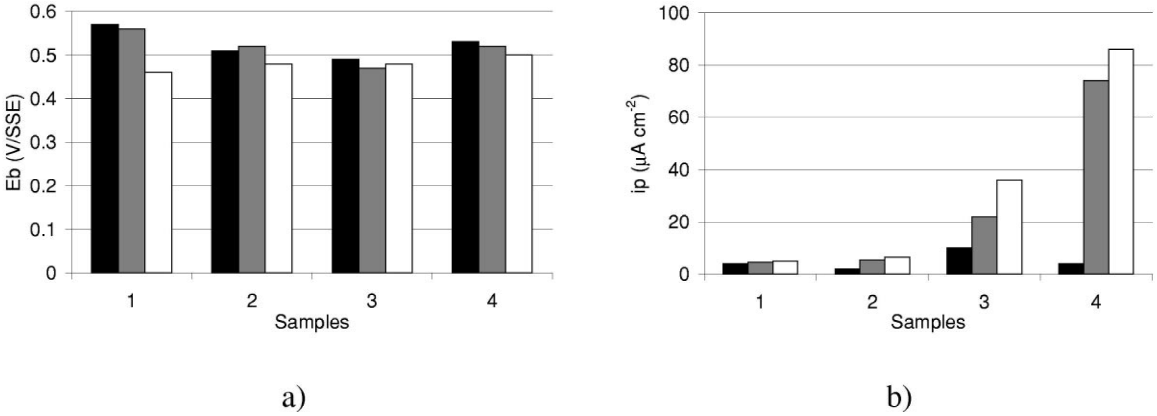


Fig. 3. Values of (a) E_b and (b) i_p for the different samples in 1 M H_2SO_4 (black), 1 M H_2SO_4+1000 ppm Cl^- (gray), and 1 M H_2SO_4+10 000 ppm Cl^- (white).

position, constitutes another point to deal with in order to get more insight on this complex matter.

The microstructure of samples 1 and 4 after the electrochemical etching in the chloride containing solution is shown in Fig. 5. Intergranular corrosion was the main phenomenon that occurred (Fig. 5a). The micrographs show remarkable difference in the depth of corrosion attack, which increases with the degree of work hardening. Dendritic structures, probably formed by the crystallisation of corrosion products in the grain boundaries, are evident in sample 4 (Fig. 5b).

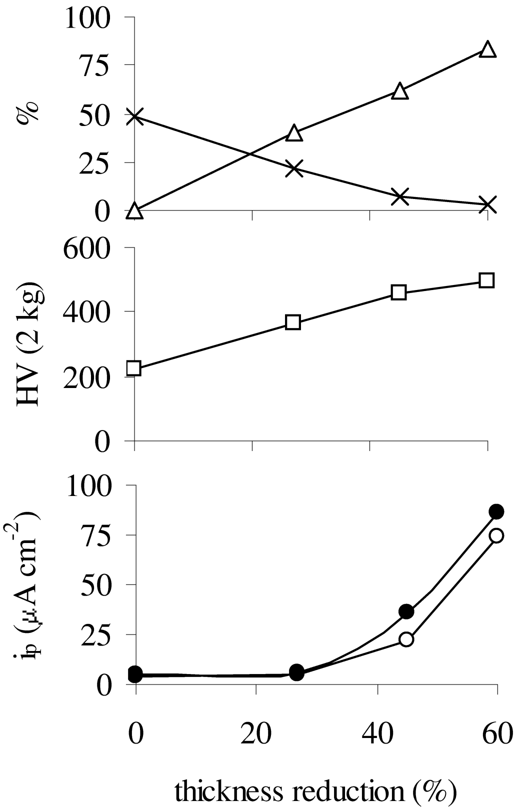


Fig. 4. Dependence of martensite content (△), $\epsilon_{50\%}$ (×), hardness (□) and passivity current (○, 100 ppm Cl^-; ●, 1000 ppm Cl^-) from thickness reduction.

4. Conclusions

Electrochemical measurements have been used to investigate the corrosion behaviour of AISI 301 in sulphuric acid in presence of chlorides. Morphological analyses have been performed to relate the electrochemical results to the alloy structure. The characteristic metastable equilibrium of the austenitic phase is highlighted. Moreover, it is shown that important changes in the microstructure (grain morphology, martensite formation and crystallographic texture . . .) are promoted by the cold working. The available results do not allow the contribution of each effect produced by cold rolling to the decay of the anticorrosive properties of the SS passive layer to be clearly pointed out. Nevertheless the increased susceptibility to corrosion of work hardened AISI 301 has been singled out and quantified.

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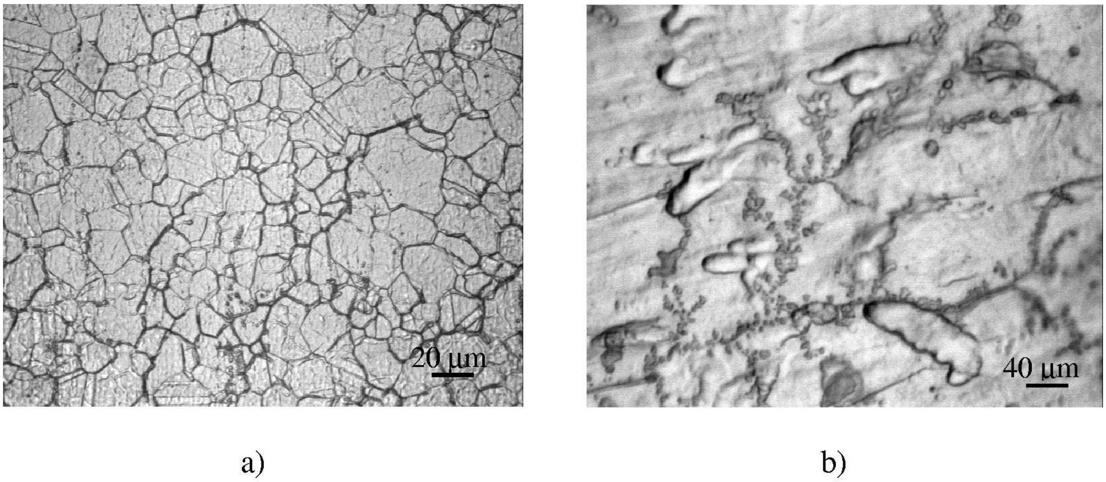

Fig. 5. Intergranular corrosion on the (a) annealed and (b) most work hardened samples after the potentiodynamic measurements in 1 M H_2SO_4 + 10 000 ppm of Cl^-.

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