Postprint: Pitting Corrosion Behavior of Ultrafine-Grained 304L Stainless Steel in Cl—-Containing Solutions

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Abstract

The pitting corrosion behavior of ultrafine-grained 304L stainless steel with a grain size of (130$±$30) nm, fabricated by equal-channel angular pressing, in a Cl—-containing solution (0.05 mol/L H2SO4+ 0.05 mol/L NaCl) was investigated using potentiodynamic polarization, cyclic polarization, electrochemical impedance spectroscopy, Mott-Schottky curves, combined with surface morphology observation. The results indicate that, compared with the coarse-grained material, the ultrafine-grained material exhibits higher corrosion current density and passivation current density, lower corrosion potential, breakdown potential, and protection potential, along with a narrower passivation region. Severe plastic deformation induces significant grain refinement in 304L stainless steel; on one hand, it increases the donor density and diffusion coefficient of the surface passive film, reduces the compactness of the passive film, and enhances Cl— adsorption on the material surface; on the other hand, it increases the grain boundary content, facilitates inward diffusion of Cl— along grain boundaries, and promotes pit nucleation and growth.

Full Text

Investigation on Pitting Corrosion Behavior of Ultrafine-Grained 304L Stainless Steel in Cl^--Containing Solution

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Abstract

The electrochemical behavior and pitting corrosion of ultrafine-grained 304L stainless steel (304L SS) with an average grain size of (130$±30)*nm, preparedbyequalchannelangularpressing*(
}−*containingsolution*(0.05*mol*/*LH{2}SO*{4}$ + 0.05 mol/L NaCl) using potentiodynamic polarization, cyclic polarization, electrochemical impedance spectroscopy (EIS), Mott-Schottky (M-S) measurements, and SEM observation of surface morphology. Compared to its coarse-grained counterpart, the ultrafine-grained material exhibited higher corrosion current density and passivation current density, lower corrosion potential, breakdown potential, and protection potential, along with a narrower passive region. Severe plastic deformation-induced grain refinement in 304L SS had two major effects: first, it increased the donor density and diffusion coefficient of the surface passive film, reducing film compactness and enhancing Cl^- adsorption capacity on the material surface; second, it increased the grain boundary content, facilitating inward diffusion of Cl^- along grain boundaries and promoting pit nucleation and growth.

Keywords: 304L stainless steel, equal channel angular pressing (ECAP), ultrafine grain, passive film, pitting corrosion

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1. Introduction

When material grain size is refined to the submicron or nanoscale, significant improvements in strength and other special physical and chemical properties can be achieved. The equal channel angular pressing (ECAP) method can reduce grain size to the submicron scale through severe plastic deformation. Breakthrough progress has been made using ECAP-prepared materials; for example, Wang et al. obtained nanostructured Cu with both high strength and 65% elongation. In recent years, the electrochemical corrosion performance of ultrafine-grained and nanocrystalline materials has attracted increasing attention from researchers worldwide. Liu et al. systematically reviewed the electrochemical corrosion properties of nanocrystalline materials, noting that grain refinement accelerates corrosion reactions in the active dissolution region but may improve corrosion resistance in the passive region by enhancing elemental diffusion and altering passive film composition.

Stainless steels form stable passive films that provide excellent corrosion resistance. However, research on bulk ultrafine-grained stainless steels prepared by ECAP remains limited due to two main factors: first, the high strength and work hardening capacity of stainless steels restrict ECAP processing; second, according to traditional corrosion theory, increased grain boundary content raises system energy and accelerates corrosion reactions. The corrosion of ultrafine-grained and nanocrystalline materials is complex, depending on both the grain refinement method and the corrosion environment. Li et al. reported that nanocrystallization significantly improved stainless steel corrosion resistance in H_2SO_4+Na_2SO_4 systems. Han et al. observed similar effects in ultrafine-grained 304L stainless steel in H_2SO_4+Na_2SO_4 solutions. Meng et al. found that grain refinement enhanced Cl^- erosion resistance in sputtered nanocrystalline Fe-Cr coatings, whereas Li et al. observed decreased Cl^- erosion resistance in ultrasonic shot-peened nanocrystalline Fe-20Cr alloys. Chloride ions exhibit strong adsorption on metal and alloy surfaces, readily inducing pitting corrosion. Research on pitting corrosion of ECAP-formed ultrafine-grained stainless steels in Cl^--containing solutions remains scarce, with considerable controversy regarding their corrosion resistance and mechanisms. This work investigates the effect of ultrafine-grained structures, formed by severe plastic deformation, on the Cl^- pitting corrosion resistance of 304L stainless steel using cast coarse-grained 304L SS as a reference.

2. Experimental

The material used was 304L stainless steel with an original grain size of approximately 50 m and chemical composition (mass fraction, %) of: Cr 18.19, Ni 8.04, Mn 1.68, Cu 0.55, Co 0.16, S 0.03, N 0.08, P 0.026, Mo 0.12, C 0.02, and Fe balance. The as-cast 304L SS (CG-304L SS) was subjected to six ECAP passes at 500 °C following route Bc (90° rotation between adjacent passes with constant extrusion direction), yielding ultrafine-grained material (UFG-304L SS) with a grain size of (130$±$30) nm.

All electrochemical tests, including potentiodynamic polarization, cyclic polarization, Mott-Schottky (M-S) curves, and electrochemical impedance spectroscopy (EIS), were performed on a PARSTAT 2273 workstation using a three-electrode system: the sample as working electrode, graphite as auxiliary electrode, and saturated calomel electrode (SCE) as reference electrode. All potentials reported herein are relative to SCE. Working electrodes were 10 mm

× 10 mm squares with Cu wires spot-welded on the back, sealed with epoxy resin, ground with SiC paper from 180 to 2000 grit, polished, rinsed, degreased with acetone, and dried. The corrosive medium was 0.05 mol/L H_2SO_4 + 0.05 mol/L NaCl solution, prepared with analytical-grade reagents and deionized water. Prior to potentiodynamic and cyclic polarization tests, samples were polarized at -0.5 V for 3 min to remove air-formed oxide films, then immersed in the test solution for 1 h. Potentiodynamic polarization was conducted at 0.5 mV/s to achieve quasi-steady-state conditions, while cyclic polarization, a transient method, was performed at 5 mV/s from 0.1 V below open-circuit potential to 1.0 V, then scanned back to open-circuit potential.

After cyclic polarization testing, surface morphology was examined using a JSM-6301F field-emission scanning electron microscope (SEM). Based on polarization results, samples were anodically polarized for 30 min at different film formation potentials (Ef) within the stable passive region to prepare passive films for M-S and EIS testing. M-S measurements were performed with 20 mV steps at 1 kHz frequency using a 5 mV amplitude sinusoidal signal over the potential range of -0.1 to 0.8 V. EIS tests were conducted at open-circuit potential with a 10 mV perturbation over the frequency range of 100 kHz to 50 mHz. All tests used a thermostatic water bath at (25$±$0.5) °C.

2.1 Effect of Ultrafine-Grained Structure on Electrochemical Corrosion Behavior of 304L SS

Figure 1 shows the potentiodynamic and cyclic polarization curves of UFG-304L SS and CG-304L SS in 0.05 mol/L H_2SO_4 + 0.05 mol/L NaCl solution, with fitting results summarized in Table 1. The potentiodynamic polarization curves of both materials exhibit similar shapes with stable passive regions, but the UFG-304L SS curve is shifted significantly downward and rightward. In the active region, UFG-304L SS shows a corrosion potential (Ecorr) of -466 mV, 65 mV more negative than CG-304L SS, and a corrosion current density (icorr) of 81.74 mA/cm^2, 4.2 times higher than CG-304L SS. In the passive region, the passive range for UFG-304L SS (-315 to 450 mV) is narrower than for CG-304L SS (-305 to 600 mV), with a passivation potential (Ep) of -315 mV (10 mV more negative) and a passive current density (ip) of 32.38 mA/cm^2, 1.6 times higher than CG-304L SS.

Figure 1b [Figure 1: see original paper] shows typical hysteresis loops for both materials, indicating pitting occurrence. The larger hysteresis loop for UFG-304L SS corresponds to a 100 mV decrease in breakdown potential (Eb) and a 190 mV decrease in protection potential (Ebp) compared to CG-304L SS. In potentiodynamic polarization, EUFG < ECG indicates lower activation energy and higher corrosion susceptibility for UFG-304L SS, while iUFG > iCG confirms faster corrosion rates. The narrower passive region and higher ip demonstrate reduced passivation performance after ultrafine-graining. In cyclic polarization, larger hysteresis loops indicate more severe passive film damage and poorer repair capability. The lower Eb and Ebp values reflect increased pitting susceptibility in Cl^--containing solutions.

ECAP processing significantly elongated and refined the 304L SS grains from 50 m to (130$±30)*nm*, *creatingnumeroushigh−anglegrainboundaries.Thesubstantialincreaseingrainboundary*
}$ solutions, consistent with traditional corrosion theory.

2.2 Effect of Ultrafine-Grained Structure on Pitting Morphology of 304L SS

Figure 2 [Figure 2: see original paper] presents SEM images of UFG-304L SS and CG-304L SS surfaces after cyclic polarization in 0.05 mol/L H_2SO_4 + 0.05 mol/L NaCl solution. The UFG-304L SS surface shows significantly more pitting pits than CG-304L SS, indicating increased pitting susceptibility and easier pit initiation in Cl^--containing solutions.

2.3 Effect of Ultrafine-Grained Structure on Carrier Density of Passive Film on 304L SS

As shown in Figure 1a, stable passive films form on both UFG-304L SS and CG-304L SS at potentials of 0.1-0.5 V in 0.05 mol/L H_2SO_4 + 0.05 mol/L NaCl solution. To examine differences in passive films, samples were polarized for 30 min at various formation potentials (Ef = 0.1, 0.2, 0.3, and 0.4 V). Figure 3 [Figure 3: see original paper] shows the M-S curves for these passive films.

Stainless steel passive films exhibit semiconductor properties, with the relationship between space charge capacitance (C) and applied potential (E) described by Mott-Schottky theory:

For n-type semiconductors:
For p-type semiconductors:

where Nd and Na represent donor and acceptor carrier densities, k is the slope of the linear C^{-2} vs. E relationship, e_0 = 8.85$×10^{-12}$ F/m is the vacuum permittivity, is the dielectric constant of the passive film (taken as 15.6 in this work), Efb is the flat-band potential, K = 1.38$×10^{-23}$ J/K is the Boltzmann constant, T is temperature, e = 1.602$×10^{-19}$ C is the elementary charge, and KT/e 25 mV at room temperature (negligible).

The positive k-values for both UFG-304L SS and CG-304L SS passive films indicate n-type semiconductor characteristics. The donor density (Nd) can be calculated from k at different Ef values, with results shown in Table 2 . At the same Ef, the donor density of UFG-304L SS passive film is approximately 1.1 times that of CG-304L SS, indicating more oxygen vacancy defects, consistent with the higher ip values. ECAP processing did not change the semiconductor type but increased carrier density, promoting passive film dissolution and reducing corrosion resistance.

2.4 Effect of Ultrafine-Grained Structure on Carrier Diffusion Coefficient in Passive Film on 304L SS

According to the point defect model (PDM), Nd and Ef follow the relationship:

where w_1, w_2, and b are constants. The diffusion coefficient (D_0) of donor defects in the passive film can be expressed as:

where J_0 is the steady-state diffusion flux of donors, G is a constant related to average electric field strength (eL) and temperature, expressed as:

where F is Faraday' s constant, R is the gas constant, T is temperature, and eL can be expressed as:

where α is the polarizability constant at the passive film/solution interface (taken as 0.45 in this work), B is a constant, and Lss is the space charge layer thickness (approximately equal to passive film thickness), expressed as:

where A is the passive film area. Using equations (4)-(9) [27,28], D_0 can be obtained by fitting Nd-Ef and Lss-Ef relationships.

Figure 4 [Figure 4: see original paper] shows the Nd-Ef data for passive films on UFG-304L SS and CG-304L SS in 0.05 mol/L H_2SO_4 + 0.05 mol/L NaCl solution. Fitting with equation (4) yields the following relationships:

$[6.19 \exp(-4.06Ef) + 3.38] \times 10^{19}$ (UFG-304L SS)
$[5.22 \exp(-5.50Ef) + 3.55] \times 10^{19}$ (CG-304L SS)

Figure 5 [Figure 5: see original paper] shows the Lss-Ef data calculated using equations (4), (6)-(10). At the same Ef, the passive film thicknesses are similar for both materials. The Lss-Ef relationship can be linearly fitted, with UFG-304L SS showing a smaller slope, indicating slower passive film growth. From equations (4)-(10) and curve fitting, the diffusion coefficients are:

UFG-304L SS surface passive film diffusion coefficient: 1.56×10^{-16} cm^2/s
CG-304L SS surface passive film diffusion coefficient: 9.73×10^{-17} cm^2/s

The D_0 for UFG-304L SS is 1.6 times that of CG-304L SS, indicating easier oxygen vacancy diffusion. Compared to CG-304L SS, the UFG-304L SS passive film has higher point defect density and stronger defect diffusion capability, both contributing to poorer corrosion resistance.

2.5 Effect of Ultrafine-Grained Structure on Compactness of Passive Film on 304L SS

Figure 6 [Figure 6: see original paper] shows Nyquist plots for passive films formed on UFG-304L SS and CG-304L SS at different Ef values in 0.05 mol/L H_2SO_4 + 0.05 mol/L NaCl solution. The EIS spectra are similar, consisting of capacitive semicircles, but UFG-304L SS shows smaller impedance magnitudes. Fitting with the equivalent circuit in Figure 6a yields the parameters in Table 3 , where Rs, Rf, and Qf represent solution resistance, passive film resistance, and passive film capacitance, respectively. The Rf values for UFG-304L SS (2.19$×10^{4}$ to 4.03$×10^{4}$ $\Omega \cdot cm^2$) are lower than those for CG-304L SS at the same Ef.

Both Figure 6 and Table 3 show that Rf increases with Ef, indicating progressively more compact and corrosion-resistant passive films. However, at any given Ef, UFG-304L SS exhibits lower Rf than CG-304L SS, demonstrating reduced passive film compactness and corrosion resistance, consistent with literature reports [29,30].

2.6 Pitting Mechanism Analysis

According to the point defect model (PDM) [24], in solutions containing aggressive Cl^-, oxygen vacancies at the film/electrolyte interface can adsorb Cl^- and react via Mott-Schottky pair reactions to generate oxygen vacancy/metal cation vacancy pairs. The generated oxygen vacancies can further react with other Cl^- ions at the film/solution interface, producing more metal cation vacancies. This autocatalytic process of metal cation vacancy formation disrupts the dynamic equilibrium of the passive film, causing dissolution without regrowth and ultimately leading to localized film breakdown and pitting [31].

Figure 7 [Figure 7: see original paper] schematically illustrates pitting corrosion for UFG-304L SS and CG-304L SS in 0.05 mol/L H_2SO_4 + 0.05 mol/L NaCl solution. In Cl^--containing acidic media, ultrafine-grained stainless steel shows significantly decreased corrosion resistance compared to conventional coarse-grained material. Two main factors contribute to this: first, severe plastic deformation substantially increases point defect density (e.g., oxygen vacancies and metal cations) in the 304L SS passive film, enhances defect diffusion capability, and reduces film compactness, all of which significantly increase Cl^- adsorption and facilitate pit nucleation and growth; second, the dramatically increased grain boundary content in ultrafine-grained materials provides fast diffusion channels, markedly enhancing inward Cl^- diffusion along grain boundaries and promoting pit nucleation.

Conclusion

Ultrafine-grained 304L stainless steel with a grain size of (130$±30)nmwaspreparedbyequalchannelangularpres
+ 0.05 mol/L NaCl solution, the ultrafine-grained 304L SS exhibited faster active dissolution, a narrower passive region, and a passive current density of 32.38 $mA \cdot cm^2$ (approximately 1.6 times that of coarse-grained 304L SS). Compared to coarse-grained material, the breakdown potential and protection potential of ultrafine-grained 304L SS shifted negatively by 100 mV and 190 mV, respectively. The donor density of the ultrafine-grained 304L SS passive film was about 1.1 times that of coarse-grained material, the defect diffusion coefficient increased by one order of magnitude, and passive film compactness decreased. The high grain boundary content in ultrafine-grained 304L SS significantly enhanced Cl^- adsorption on the surface and short-circuit diffusion

along grain boundaries, making pitting corrosion more likely to occur.

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