Electrochimica Acta 54 (2009) 1618–1629

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Effects of cold work and sensitization treatment on the corrosion resistance of high nitrogen stainless steel in chloride solutions

Yao Fu [a], Xinqiang Wu [a,*], En-Hou Han [a], Wei Ke [a], Ke Yang [a], Zhouhua Jiang [b]

[a] *State key Laboratory for Corrosion and Protection, Institute of Metal Research, South Campus, Chinese Academy of Sciences, 62 Wencui Road, Shenyang 110016, PR China*
[b] *School of Materials and Metallurgy, Northeastern University, Shenyang 110004, PR China*

ARTICLE INFO

Article history:
Received 31 July 2008
Accepted 24 September 2008
Available online 8 October 2008

Keywords:
High nitrogen stainless steel
Cold work
Sensitization treatment
Corrosion resistance
X-ray photoelectron spectroscopy

ABSTRACT

The effects of cold work and sensitization treatment on the microstructure and corrosion resistance of a nickel-free high nitrogen stainless steel (HNSS) in 0.5 M H_2SO_4 + 0.5 M NaCl, 3.5% NaCl and 0.5 M NaOH + 0.5 M NaCl solutions have been investigated by microscopic observations, electrochemical tests and surface chemical analysis. Cold work introduced a high defect density into the matrix, resulting in a less protective passive film as well as reduced corrosion resistance for heavily cold worked HNSS in a 3.5% NaCl solution. No obvious degradation in corrosion resistance took place in a 0.5 M H_2SO_4 + 0.5 M NaCl solution, possibly due to the stability of the passive film in this solution. Sensitized HNSSs showed reduced corrosion resistance with increasing cold work level in both 3.5% NaCl and 0.5 M H_2SO_4 + 0.5 M NaCl solutions due to a reduction in the anti-corrosion elements in the matrix during the cold work-accelerated precipitation process. The cold work and sensitization treatment had no influence on the corrosion resistance of the HNSS in the 0.5 M NaOH + 0.5 M NaCl solution even though the property of the passive film changed. The effects of cold work and sensitization treatment on the characteristics of passive films formed in the three solutions are discussed.

1. Introduction

The beneficial effects of nitrogen on the properties of high-alloyed steels have led to the widespread development of high nitrogen stainless steels (HNSSs) due to recent advances in processing technologies [1–3]. As an alloying element, nitrogen has several beneficial effects on the properties of steels, in particular, those related to high yield strength and toughness (good fracture resistance) [1]. Nitrogen is also a strong austenite-stabilizing element and can thus substitute for nickel, which is expensive and causes an allergic reaction in human skin. Moreover, nitrogen alloying, especially in combination with molybdenum, improves resistance to localized corrosion in general, and resistance to general corrosion in some environments [4,5].

One problem with HNSS is the formation of precipitates such as Cr-nitride, σ, and χ upon thermal exposure in the temperature range of 500–1050 °C, leading to a significant reduction in corrosion resistance [6,7]. It has been reported that the deleterious effects of Cr_2N on pitting corrosion are associated with the formation of a Cr-depletion zone adjacent to Cr_2N precipitates [8]. It was also found that the lamellar Cr_2N was the most susceptible site for pitting corrosion when compared with any other heterogeneity or Cr_2N precipitate along the grain boundaries [9]. Stainless steels are subject to different levels of cold work during the final manufacturing stages of components for numerous applications in industry. Cold work might affect the corrosion resistance of stainless steels because deformed substructures like planar dislocation arrays [1,7] and deformation twinning [10] could be introduced. Peguet et al. [11] have reported the different roles of cold work on the pitting corrosion resistance at different pitting stages, including pit initiation, propagation and repassivation. Barbucci et al. [12] reported that the passive currents of 304 SS in sulfate + chloride solutions significantly increased with the degree of cold work. In addition, the pitting corrosion resistance was observed to decrease with increasing cold work in a 3.5% NaCl solution [13]. Efforts have also been made to clarify the relationship between cold work and the sensitization process. The cold work effect in Type 316 SS has been determined to be due to the higher diffusivity of chromium and the lower free energy barrier to carbide nucleation at grain boundaries in the deformed microstructure [14–17]. The acceleration of sensitization with cold work could also be related to the effects of

* Corresponding author. Tel.: +86 24 23841883; fax: +86 24 23894149.
E-mail address: xqwu@imr.ac.cn (X. Wu).

0013-4686/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2008.09.053

point defects and microstructural sinks on diffusion, as reported by Mansur [18].

The metallurgical changes caused by cold work and sensitization treatment have not been related clearly to the influence on the corrosion resistance in chloride solutions of different pH. Moreover, previous studies have not included the composition and structural evolution of passive films, which have direct influence on the corrosion resistance.

In the present work, we examine the microstructure and corrosion resistance of a HNSS after cold work and/or sensitization treatment. The structural and chemical composition of the passive film induced by cold work and sensitization treatment were analyzed by electrochemical impedance spectroscopy (EIS), and X-ray photoelectron spectroscopy (XPS). The morphology of the pitting attack after electrochemical polarization was observed. The relationship between the microstructure evolution, changes in passive film characteristics and variations in the corrosion resistance of the HNSS are discussed.

2. Experimental

2.1. Microstructure observation

The chemical composition of the HNSS investigated is listed in Table 1. The steel plates were cold rolled to a 8, 30, 49 or 60% reduction in thickness. Some of the specimens were then isothermally sensitized at 650 °C for 2 h. 10 mm × 10 mm specimens were cut from the plates, with test surfaces parallel to the rolling direction. The specimens were polished to a diamond finish (1.5 μm) and electrolytically etched in a 10% ethane diacid reagent at 12 V for 90 s to observe the changes in microstructure introduced by cold work.

Specimens for transmission electron microscopy (TEM) analysis were mechanically polished and punched into 3 mm discs. Final thinning was performed using a twin-jet electrolytic polisher operated at 20 V in an electrolyte of perchloric acid and alcohol at −30 °C. The substructure of the cold worked and sensitized specimen was analyzed by an FEI Tecnai G2 F20 S-Twin microscope.

Table 1
Chemical composition of the high nitrogen stainless steel in this work (in wt.%).

C	0.04
Cr	18.4
Mn	15.8
Mo	2.19
N	0.66
Si	0.24
S	0.005
P	0.017
Fe	Bal

2.2. Electrochemical tests

2.2.1. Electrodes and electrolyte

To prepare working electrodes for the electrochemical tests, the specimens were sealed with an epoxy resin to expose an area of 1 cm^2. The exposed faces were polished with 800 grit silicon carbide paper and rinsed with de-ionized water just before immersion. The specimens used to observe pitting attacks after polarization tests were polished to a diamond finish (1.5 μm). After immersion for 5 min, the working electrode was passivated at the film formation potential for 20 min for EIS measurements and 1 h for XPS measurements, respectively. A three electrode cell featuring a Pt counter electrode and a saturated calomel reference electrode (SCE) was employed. All the potentials in the paper are given vs. this reference electrode. The solutions used in this investigation were: solution I, 0.5 M H_2SO_4 + 0.5 M NaCl (pH ≈ 0.4); solution II, 3.5% (0.6 M) NaCl (pH ≈ 5.8); and solution III, 0.5 M NaOH + 0.5 M

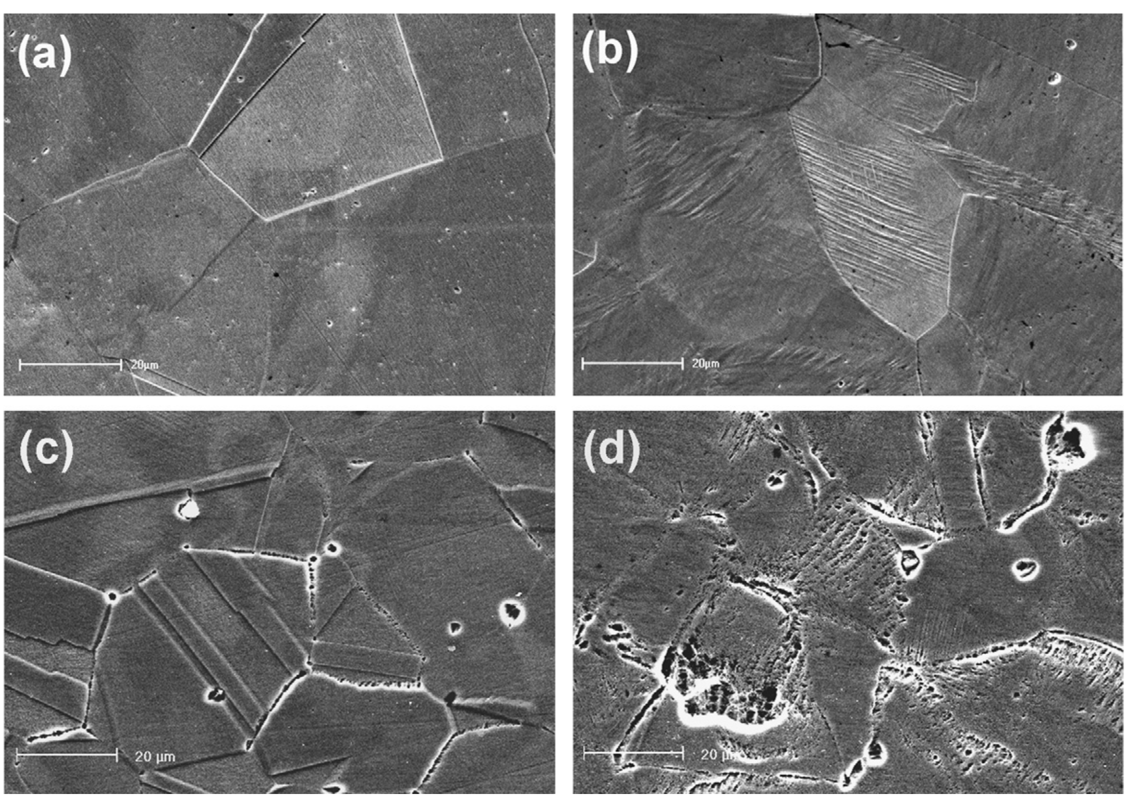

Fig. 1. SEM images of (a) deformation bands in an 8% cold worked non-sensitized HNSS, (b) deformation bands in a 30% cold worked non-sensitized HNSS, (c) weakened grain, twin boundaries in an 8% and also (d) deformation bands in a 30% cold worked sensitized HNSS.