ARTICLE IN PRESS

Corrosion Science xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Corrosion Science

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

Influence of the microstructure on the corrosion behaviour of low-carbon martensitic stainless steel after tempering treatment

V. Vignal [a,c,*], S. Ringeval [b,c], S. Thiébaut [b,c], K. Tabalaiev [a,c], C. Dessolin [a,b], O. Heintz [a,c], F. Herbst [a,c], R. Chassagnon [a,c]

[a] ICB, UMR 6303 CNRS-Université de Bourgogne, BP 47870, 21078 Dijon, France
[b] CEA, DAM, centre d'études de Valduc, 21120 Is-sur-Tille, France
[c] Laboratoire Interactions Matériau-Procédé-Environnement, LRC LIMPE n° DAM-VA-11-02, France

A R T I C L E I N F O

Article history:
Received 28 January 2014
Accepted 28 March 2014
Available online xxxx

Keywords:
A. Stainless steel
C. Pitting corrosion

A B S T R A C T

The microstructure of grade X4CrNiMo16.5.1 stainless steel was studied at different scales. The chemical composition of the native passive film formed on the different phases was then determined at the micro-scale. The degree of homogeneity of the native passive film is discussed. Subsequently, the susceptibility to pitting corrosion of X4CrNiMo16.5.1 was quantified using the electrochemical microcell technique. The nature of precursor sites and the morphology of pits were investigated by combining scanning electron microscopy with Electron BackScatter Diffraction and potentiostatic pulse tests. The role of the microstructure and the cold-worked layer generated by polishing in pitting is discussed.

1. Introduction

Grade X4CrNiMo16.5.1 steel is a low-carbon martensitic stainless steel. It is an important engineering material that combines excellent mechanical properties, reasonable corrosion resistance and good weldability. This metallic alloy is used in various sectors, such as the marine [1], chemical and petrochemical industries and in aeronautics [2,3]. Grade X4CrNiMo16.5.1 stainless steel has a complex microstructure. It generally contains 80–90% martensite when quenched and tempered, with ~5–10% retained austenite and ~5–10% ferrite. Martensite laths are a characteristic structure in quenched steels with low carbon content.

Many studies have been conducted on the morphology and crystallography of lath martensite [[4,5] and ref therein]. It has been pointed out that these two characteristics play an important role in the mechanical behaviour of martensitic stainless steels. For instance, electron backscattered diffraction (EBSD) patterns have been used [6] to investigate the relationships between the local deformation behaviour and crystallographic features (in terms of slip system activities) in as-quenched lath martensite of low-carbon steel during uniform elongation in tensile tests.

On the other hand, only a few papers have been devoted to the corrosion behaviour of grade X4CrNiMo16.5.1 stainless steel under strain conditions [7,8]. Initiation and early growth mechanisms of corrosion fatigue cracks in grade X4CrNiMo16.5.1 stainless steel have been studied in various NaCl media [8]. When the material was passive (no pitting corrosion), corrosion fatigue cracks were found to occur exclusively at oxide inclusions. It has been proposed that an inclusion-matrix debonding mechanism is the preliminary step leading to the crack nucleation. This debonding is promoted by preferential dissolution at the interface. With increasing temperature and/or chloride concentration, it has been found that corrosion mainly occurs during crack propagation.

Until now, to our knowledge, no studies have been devoted to the pitting corrosion behaviour of grade X4CrNiMo16.5.1 stainless steel. Therefore, there are still open questions concerning the relationships between the specimen microstructure, the passive properties of the alloy and the corrosion mechanisms. However, some interesting results have been obtained on austenitic stainless steels containing martensite after cold-working. It has been demonstrated [9,10] that the presence of strain-induced martensite is not a necessary condition for the susceptibility of cold worked stainless steels to pit initiation in NaCl media. It has been shown that pit initiation is more likely to be related to dislocation pile-up. In solutions containing sulphate and chloride ions [11], the increased susceptibility to pitting corrosion of the work-hardened samples has been explained by the formation of a much more defective oxide. The growth of such an imperfect oxide is related to the formation of defects in the grains and at interfaces, which results from the accumulation of internal stresses during cold-rolling.

---

* Corresponding author at: ICB, UMR 6303 CNRS-Université de Bourgogne, BP 47870, 21078 Dijon, France. Tel.: +33 0 380 39 6160; fax: +33 0 380 39 6132.
E-mail address: vincent.vignal@u-bourgogne.fr (V. Vignal).

http://dx.doi.org/10.1016/j.corsci.2014.03.036
0010-938X/© 2014 Elsevier Ltd. All rights reserved.

Please cite this article in press as: V. Vignal et al., Influence of the microstructure on the corrosion behaviour of low-carbon martensitic stainless steel after tempering treatment, Corros. Sci. (2014), http://dx.doi.org/10.1016/j.corsci.2014.03.036

In the present paper, the specimen microstructure and the chemical composition/thickness of the native passive film formed on grade X4CrNiMo16.5.1 stainless steel after tempering were first studied at the microscale. The corrosion behaviour was then investigated in NaCl-based media, both at the micro and macroscale. Finally, the electrochemical response was analysed considering the specimen microstructure (nature of phases, presence of defects, dislocation pile-up…) and the characteristics of the native passive film.

2. Experimental

2.1. Specimens and surface preparation

Experiments were performed on grade X4CrNiMo16.5.1 stainless steel (average chemical composition: Cr: 15.48 wt.%; Ni: 4.75 wt.%; Mo: 0.97 wt.%; Mn: 0.93 wt.%; Si: 0.24 wt.%, Cu: 0.10 wt.%, C: 605 wt ppm, $S < 20$ wt ppm). Specimens first underwent a thermal treatment at 1040 °C (formation of austenite), followed by oil quenching and a tempering treatment at 570 °C for 4 h. The objective of this treatment was to obtain a good compromise between a high yield strength and good toughness. Specimens were then ground with silicon carbide (SiC) papers down to 4000 grit and polished with diamond pastes (6, 3 and 1 μm).

2.2. Surface observations and electron microscopy studies

A field emission scanning electron microscope (JEOL JSM-6400F) with an in-built energy dispersion spectrometer (FE-SEM/EDS) was used to determine the morphology and the chemical composition of inclusions and ferrite islands at the microscale.

Transmission Electron Microscopy was used to determine the chemical composition of the matrix. These studies were carried out at the microscale using a JEOL JEM-2100 microscope with a LaB_6 source operating at 200 kV. This equipment was used in the

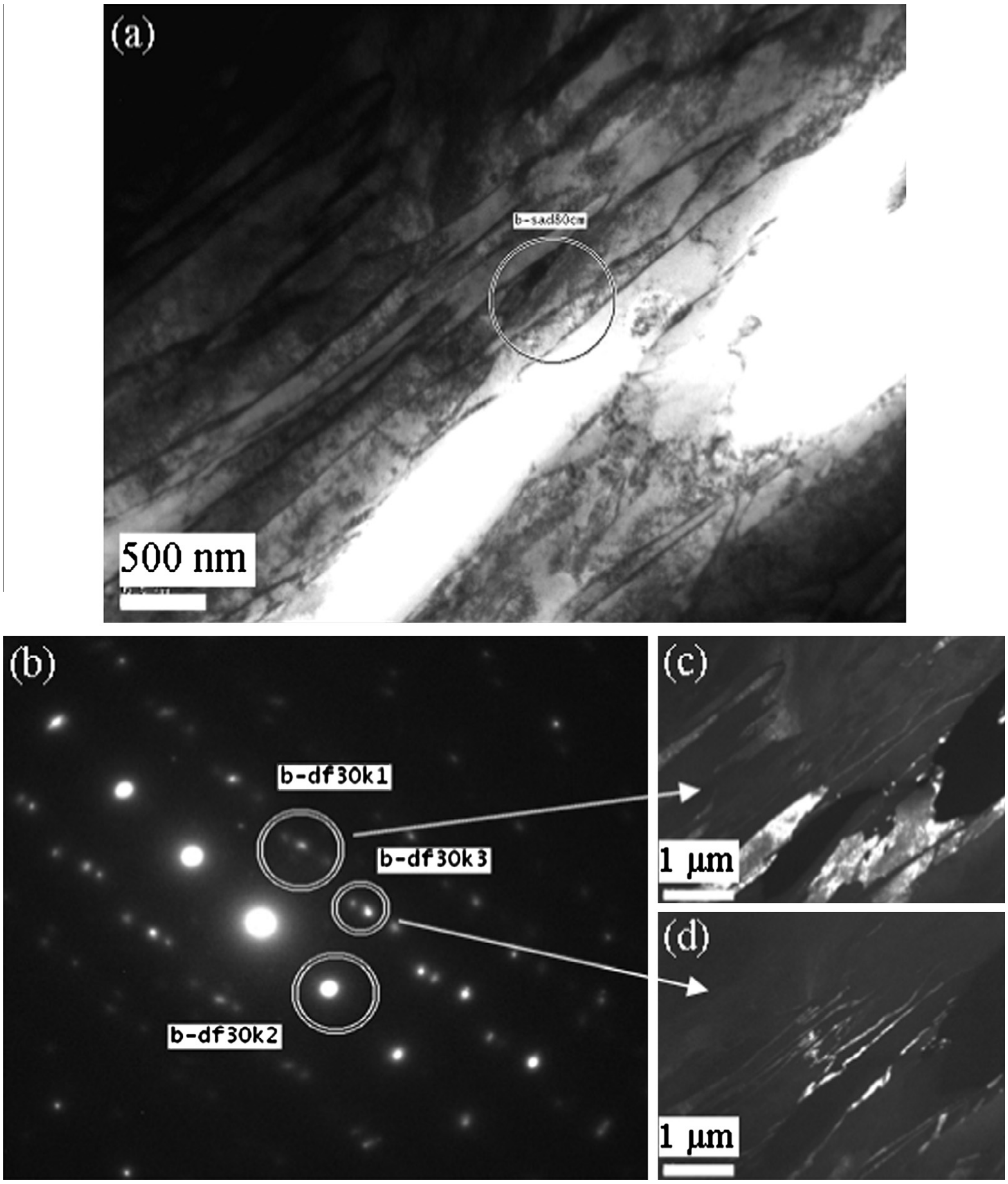

Fig. 1. (a) TEM bright field image of the grade X4CrNiMo16.5.1 microstructure. (b) Selected Area Diffraction (SAD) pattern acquired on both martensite and austenite within the circle shown in (a). Dark field images of (c) the martensite laths and (d) the austenite between laths.

Please cite this article in press as: V. Vignal et al., Influence of the microstructure on the corrosion behaviour of low-carbon martensitic stainless steel after tempering treatment, Corros. Sci. (2014), http://dx.doi.org/10.1016/j.corsci.2014.03.036