



Mechanical and electrochemical behavior of nanocrystalline surface of 304 stainless steel

X.Y. Wang*, D.Y. Li

Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta, Canada T6G 2G6

Received 27 March 2002; received in revised form 18 June 2002

Abstract

This paper reports our recent studies on nanocrystalline surface layer of 304 stainless steel (304SS) produced using a sandblasting and annealing process. The grain size of the sandblasted surface layer was less than 20 nm. Mechanical and electrochemical properties of the nanocrystalline surface and its passive film were investigated using nano/micro-indentation, micro-scratch, scanning Kelvin probe (SKP), potentiodynamic scanning and electrochemical scratch techniques. It was demonstrated that the nanocrystalline surface was markedly superior to that of original 304SS with enhanced passive film. The polarization, electrochemical scratch and SKP measurements indicated that the nanocrystalline surface had higher resistance to corrosion, greater capability of repassivation and higher chemistry stability. All results demonstrated that the nanocrystallization surface did not only enhance the mechanical properties of the surface layer and its passive film, but also benefited the passivation capability of the steel with improved corrosion resistance. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Nanocrystallization; Sandblasting; Corrosion; Mechanical properties; Passive film

1. Introduction

Efforts have been continuously made to improve existing materials and to develop new ones which are stronger, lighter, and more resistant to aggressive environments. In recent years, nanocrystalline materials have received considerable interest [1,2]. Their high hardness, improved toughness and superior physical properties have found increasing applications. However, the effect of the nanostructure on the material corrosion resistance has not been well understood although it has been reported that the nanostructured materials exhibit improved corrosion resistance. For example, Ti-implanted H13 steel shows high corrosion resistance due to the formation of nano-scale FeTi₂ phase [3]. Studies have also demonstrated that nanocrystalline Ni made by electrodeposition offers superior resistance to localized corrosion [4]. However, the mechanism responsible for such improvement has not been well understood yet.

How a nanocrystalline structure of an alloy influences its passivation behavior and properties of its passive film need to be answered.

It is well known that the corrosion resistance of a passive alloy is attributed to the formation of a protective passive film on its surface. The corrosion resistance and electrochemical behavior of passive films on different materials have been widely investigated. It has become possible to evaluate the mechanical properties of passive films thanks to the development of advanced instruments, such as atomic force microscope (AFM) and nanomechanical test instruments [5–7].

The objective of this work is to evaluate the mechanical and electrochemical properties of a nanocrystalline surface of 304 stainless steel (304SS) produced by sandblasting and annealing treatment. In particular, properties of the passive film on the nanocrystalline 304SS' surface were investigated.

2. Experiment

Specimens having their dimensions of 10 mm in diameter and 5 mm in thickness were machined from a

* Corresponding author. Tel.: +1-780-492-5157; fax: +1-780-492-2881

E-mail address: xuanyi@ualberta.ca (X.Y. Wang).

commercial 304 stainless steel (304SS) (wt.%, C, 0.08; Mn, 2.0; Si, 1.0; P, 0.04; S, 0.03; Cr, 19.0; Ni, 9.0). The surface of the specimens was polished with 600# grit paper, and then blasted by a sand flow of silica particles of 50–70 mesh under 200 kPa for 10 min. The sandblasted specimens were annealed at 350 °C for 60 min. Surfaces of the specimens were polished with alumina particles of 0.05 μm to make them as smooth as possible before testing. Before electrochemical test, a specimen was mounted using epoxy with its surface (Φ , 10 mm) under study exposed to a corrosive medium. The corrosive medium was a 3.5% NaCl solution. For comparison, the as-received and sandblasted specimens were also tested.

Polarization measurement was carried out using a commercial apparatus made by Camry Ltd. During the measurement, a saturated calomel electrode (SCE) was used as the reference electrode, and the platinum plate (Pt) was used as the counter electrode. All electrochemical tests were performed at room temperature.

The performance of the specimens during electrochemical scratch was evaluated using an apparatus that has been described in a previous paper [8]. During the test, a specimen immersed in a corrosive solution was scratched under an applied potential. In this study, two applied potentials were used, which were 50 and 100 mV (SCE) above the free corrosion potential of the specimens in the corrosion medium (E_{corr}), respectively. A diamond tip was used to scratch the surface of a specimen under a normal load, and corresponding changes in current were recorded. For the present study, the applied normal load was 20 g and the tip moving velocity was 8 mm s⁻¹. The duration of scratching was 0.25 s.

A scanning Kelvin probe (SKP) was used to measure the surface electron work function (EWF) of the specimens, which reflected their surface electrochemical stability. A gold tip with its diameter equal to 1 mm was used, and the scanning area was 2 × 2 mm. Average EWF values were obtained by measuring 100 points within in the scanning area for each surface. The EWF tests were carried out in open air.

Mechanical properties of passive films on various specimens were evaluated using a triboscope—a combination of a nanomechanical probe and an AFM. The probe was a four-sided pyramidal Vickers indenter made of diamond. During the nanoindentation test, the force–depth curve was recorded. A maximum force of 50 μN was used for the indentation test. Hardness and elastic behavior of the passive films were evaluated based on obtained force–depth curves.

The failure resistance of the passive films was evaluated using a universal micro-tribometer (UMT), which had a mechanical probe made of tungsten carbide. During the test, a surface was scratched under a normal load that was increased linearly from 0 to 20 g.

Under the applied load, the tip scratched the surface at a velocity of 0.02 mm s⁻¹. During scratching, changes in the contact electrical resistance (CER) with respect to the load were recorded. When the passive film failed under a critical load, the CER dropped steeply. The critical load reflects the resistance of a passive film to failure. Critical loads for passive films on different specimens were measured.

Surface microstructures of the sandblasted and sandblast-annealed specimens were observed under a transmission electron microscope (JEOL 2000FX2, operated under 200 kV). Zones at different distances from the sandblasted surface were observed. Surface chemical compositions of the specimens were determined using an energy dispersive spectrometer (EDS) attached to a scanning electron microscope (HITACHI S-2700). The surface mechanical properties were measured using a micro-indenter (made by Fischer Technology Inc.). The micro-indentation test was performed under a maximum load of 100 mN. Load–depth curves of micro-indentation were determined, from which the surface mechanical properties were evaluated.

3. Results and discussion

3.1. Surface analysis by TEM and EDS

Surface of 304SS was modified by sandblasting and annealing for nanocrystalline structure. The modified surface was examined using TEM. Fig. 1(a) presents TEM micrograph of the layer about 5 μm away from the sandblast-annealed surface. As shown, the size of roughly equiaxed grains in this layer was approximately 20 nm. With an increase in depth, the grain size increased. The grain size was about 100 nm in a transition zone adjacent to the unaffected inner layer as shown in Fig. 1(b). The nano-grains were randomly oriented as indicated by the selected area diffraction patterns in Fig. 1. Typical microstructure of sandblasted surface without annealing is shown in Fig. 2. The blasted surface consisted of heavily deformed grains with size about 20 nm. The TEM observation showed that the annealing treatment did not significantly change the size of grain in the sandblasted surface layer, which should, however, diminish the dislocation density of the surface layer.

The chemical compositions of the sandblasted, sandblast-annealed and the original 304SS surfaces were determined using EDS. No significant difference in compositions between surfaces of the specimens was observed. The EDS analysis results are presented in Table 1.