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ELECTROCHIMICA

Electrochimica Acta 52 (2007) 7796-7801

www.elsevier.com/locate/electacta

Influence of laser surface hardening on the corrosion resistance of martensitic stainless steel

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Received 25 July 2006; received in revised form 17 January 2007; accepted 3 February 2007

Available online 13 February 2007

Abstract

Martensitic high nitrogen stainless steels offer a combination of wear-, corrosion- and fatigue properties. But for some applications a higher surface hardness is required. A laser hardening with rapid heating (without smelting) and cooling (quenching) rates can improve the surface hardness with compressive residual stresses in the near surface layer. Yet, some cases of pitting corrosion in chloride media are reported.

In this study, the influence of process parameters, composition of the atmosphere and the overlapping ratio, has been investigated. With complementary surface analytical methods and electrochemical techniques the relation between surface structure and composition and corrosion behavior in chloride media has been studied.

It has been shown that, during the laser treatment the surface must be shielded with argon in order to avoid the formation of a porous layer of iron oxides, which is dramatically detrimental to the corrosion resistance.

After the laser treatment a mixture of martensite and retained austenite is obtained, depending on the surface temperature and overlapping ratio. With a surface temperature of $1200 \,^{\circ}$ C and a minimal overlapping ratio (10%), a thin surface layer of retained austenite, wherein nitrides are dissolved, improves the corrosion resistance. The hardness increases with the amount of distorted martensite and reaches a maximum at $1000 \,^{\circ}$ C. © 2007 Elsevier Ltd. All rights reserved.

Keywords: Martensitic stainless steel; Nitrogen; Laser hardening; Corrosion

1. Introduction

For many applications surface properties as hardness, wear and corrosion resistance are required, combined with toughness and fatigue resistance. Carburized steel is up to now a very popular material for bear and gear parts in aerospace industry. Yet, due to the quenching after the surface treatment, deformations of the pieces occur and a further rectification is needed.

Nitriding is a promising surface treatment of carbon steel in order to obtain the required mechanical properties in the bulk and at the surface of the material [1,2]. During the treatment nitrogen atoms diffuse into the steel surface (diffusion layer) and very hard nitrides (white layer) can be formed at the metal surface [3]. The treatment occurs at low temperature (about 600 $^{\circ}$ C) and no quenching is required afterwards. The barrier properties of the

white layer improve definitely the corrosion behavior of nitrided steel. Nevertheless due to its high brittleness the white layer can present cracks or even be pulled away leading to a decrease of the corrosion resistance (a possible galvanic corrosion can occur in case of cracks in this layer [4]).

Another approach consists in the choice of stainless steels for their specific mechanical bulk properties and mainly for their excellent corrosion resistance.

Martensitic high-nitrogen stainless steels (MHNS) combine tribological, mechanical and corrosion properties due to the fine dispersion of nitride and carbonitride precipitates in the martensitic matrix and to the high concentration of Cr, N and Mo in solid solution. However, for some industrial applications a still higher surface hardness is required. Laser surface hardening has been used to improve wear and fatigue resistance of steel components. Due to the rapid local heating and especially rapid cooling a quenching occurs in situ. This method is mainly used for ferrous alloys which undergo martensitic transformation [5–7]. In the literature several studies concerning laser treatments of austenitic stainless with surface melting can be found [8–12]

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Table 1Chemical composition of X30CrMoN15

С	0.275
Cr	15.0
Mo	1.0
Ν	0.350
Fe	Bal.

but less attention has been paid to the laser treatment of MHNS without melting of the metal [13–16]. It has been shown that the, during the laser treatment, generated new martensite with compressive residual stresses increases the fatigue and the sliding wear resistance but has a detrimental influence on the pitting corrosion resistance [13,14].

In this paper, the influence of the process parameters of laser treatment of MHNS is studied on the surface structure and composition, surface hardness, electrochemical characteristics and corrosion resistance in chloride media.

2. Experimental procedure

2.1. Materials and laser treatment

The chemical composition of the MHNS (X30CrMoN15) is given in Table 1.

Before the laser treatment the MHNS is heat treated to obtain a martensitic microstructure with less than 2% retained austenite (as represented in Fig. 6d) and a hardness of 40 HRc. Afterwards the samples are laser treated (at the Flemish Institute for Technological Research, VITO, Mol, Belgium) using a diode laser. The power of the laser (2–3 kW) was controlled by the maximum surface temperature (measured with a LASCON pyrometer) in the heat treated area (1200 ± 10 °C). The beam had a cross-section of 8 mm × 4 mm and was moved with a speed of 125 mm/min over the surface under an atmosphere of air or nitrogen.

The quenching rate is estimated to be about 6000 K/s. Samples were prepared with only one laser track, with an overlapping ratio of 10% and 50% (Fig. 1). The surface of the samples is cleaned with acetone before the laser treatment.

2.2. Characterization of the samples

Microstructural studies of the treated surfaces and crosssections were performed with the aid of an optical microscope (LEITZ, Metallovert) after etching with Nital or Kalling no. 1 (1.5 g CuCl₂, 33 ml HCl, 33 mL ethanol, 33 mL H₂O). Kalling no. 1 etching makes the difference between not attacked austenite and dark martensite [17]. Knoop microhardness profiles, using a load of 200 g, were performed with a STRUERS DURAMIN 1. The Knoop values are converted in HRc [18].

XPS measurements were performed with a PHI 1600 equipment using a standard Al K α X-ray source (15 kV, 350 W) and a hemispherical electron energy analyzer offering a maximal resolution of 0.8 eV. The spectra were deconvoluted with multipak V from PHI.

FEG–SEM observations were performed using FE-SEM JEOL JSM 7000F with a working distance of 10 mm and 15 keV electron beam energy.

The electrochemical experiments were performed at room temperature in a non-deaerated 0.5 M NaCl solution. Open circuit potentials (OCP) were measured versus a Ag/AgCl electrode. Polarization curves were recorded with an Autolab Instrument of Ecochemie PGSTAT10 potentiostat at a scan rate of 0.2 mV s^{-1} . The exposed area of the working electrode was 28 mm^2 (diameter: 6 mm) and could be located within the width of a track (8–10 mm), a platinum mesh and a saturated Ag/AgCl electrode were used, respectively as counter and reference electrode. The data were acquired by a Compaq Prolinea 4/66 computer, using the software program GPES developed by Ecochemie.

3. Results and discussion

3.1. Characterization of the laser treatment with one laser track in air atmosphere

As reference a sample of X30CrMoN15 has been treated with one laser track, in air and with a temperature of $1200 \,^{\circ}C$ ($\pm 10 \,^{\circ}C$) at the surface. Fig. 2a shows a cross-section of the



Fig. 1. Scheme of laser surface treatment showing the area of the laser beam, width and depth of a cross-section of the heated zone in the case of one track, an overlapping ratio of 10% and 50%. Arrows indicate the pathway followed by the laser beam.

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