Effect of anodic potential on the electrochemical response of passive layers formed on the surface of coarse- and fine-grained pure nickel in borate buffer solutions

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ABSTRACT

In the present work, the role of cold deformation and anodic potential on the electrochemical response of pure nickel in borate buffer solutions were investigated. The application of cold deformation gave rise to a more localized microstructure that contained a greater number of fine grains. In order to investigation of the electrochemical response of specimens, potentiodynamic polarization (PDP), electrochemical impedance spectroscopy (EIS), and Mott–Schottky (M–S) analysis were performed. As a result, with increasing of applied potential, the polarization resistance and passive film thickness decreased. Also, density of electron acceptor at passive layer decreased by increasing of applied potential.

1. Introduction

Various methods for enhancement of the corrosion resistance of metals and alloys have been developed within the past three decades. Some of the most interesting and important of them, involve the passivity phenomenon and with so called passive metals. Such widespread interest was provoked by the complexity and practical importance of passivity for increasing the corrosion resistance of metals and alloys [1]. The general opinion expressed in the scientific literature clearly indicates that not all cases of improved corrosion behavior can be considered as being caused by passivity. Analysis of numerous examples of passivity shows that in all cases of improved corrosion resistance, there is a sharp increase in inhibition of the anodic process. Therefore, it is logical to define passivity on the basis of the controlling factor in the corrosion system [2]. The most fundamental and generally accepted theories of passivity at present are those explaining the passive state on the basis of a film or an adsorption mechanism accounting for inhibition of anodic dissolution [3,4]. They describe improved corrosion behavior through the formation of a protective oxide layer on the surface of a metal. This layer is usually thin, transparent, and consists of the metal oxide compound.

It is well known that a reduction in the grain size of a pure metal or alloy will influence the mechanical properties of the bulk material. The work of Hall [5] and Petch [6] resulted in the relation of the yield strength of a polycrystalline material to its grain size. In other words, significant gains in strength can be generated simply by reducing grain size. This increase in the strength is attributed to dislocation pile-ups. In fact, the greater number of grain boundaries resulting from grain refinement act as extra barriers to dislocation motion and causes dislocations to pile up against the grain boundaries [7,8]. Other mechanical properties, including hardness, coefficient of friction, and wear resistance, also benefit from grain refinement. Despite the positive role of grain refinement operation on the mechanical behavior of metals and alloys has been confirmed, yet, its effect on the electrochemical response is not straightforward and rather a complex relation.

Nickel is one of the main building blocks of several commercial alloys, which are mostly used in applications that corrosion resistance is essential. Therefore, the anodic dissolution of nickel and its passive response has received a certain amount of attention [9,10]. The typical anodic potentiostatic curve in aqueous electrolytes shows that nickel dissolution occurs in an active of region but is

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inhibited at more anodic potentials. The oxide layer is accepted to inhibit nickel dissolution by forming a protective barrier between the metal and solution [11,12]. Possibly the earliest investigation of the mechanism of the anodic oxidation of nickel is that of Sato and Okamoto [13] which indicates that the film thickness is proportional to the potential. Later MacDougall and Cohen [14,15] suggested a linear relation between film thickness and potential because the electric field strength is inversely proportional to film thickness. The response of passive film to the mentioned parameters is related to the microstructure of metals. The microstructure is, in turn, a function of the processing technique. Regardless of the environment, there is some agreement that nano-grained nickel alloys are less prone to localized corrosion near grain boundaries when compared to their coarse-grained (CG) counterparts [16]. However, as Estrin and Vinogradov [17] and Miyamoto [18] emphasized, there is still no detailed understanding of the improvement of corrosion resistance in fine-grained (FG) materials.

Available research works in the field of passivation behavior of nickel has not presented a comprehensive study of the influence of cold deformation on the electrochemical response of pure nickel in media such as borate buffer solutions. Therefore, in this work, the role of anodic potential on the electrochemical response of passive layers formed on the surface of CG and FG pure nickel in borate buffer solutions was studied by potentiodynamic polarization (PDP), electrochemical impedance spectroscopy (EIS) and Mott–Schottky (M–S) analyses. Moreover, assessment of microstructure was achieved by X-ray diffraction (XRD) and optical microscope.

2. Experimental procedure

2.1. Grain refinement process

The as-received nickel (99.7 wt.%) was used as starting materials in this study. It was cut into 100 mm × 50 mm × 0.8 mm pieces, parallel to the sheet rolling direction (RD). Then, the strips were annealed at 973 K for 7200 s and furnace cooled. We rolled the specimens in the rolling direction at room temperature for 50% reduction in thickness. For all experimental tests, two specimens including annealed pure nickel as the CG sample and 50% cold worked (CW) pure nickel as the FG sample were chosen.

2.2. Microstructure observation

In order to perform phase analysis before and after cold deformation, XRD (Rigaku, Japan) analysis, operating at 40 kV and 40 mA with CuKα radiation ($\lambda = 0.1506$ nm) was used. The XRD patterns were obtained in the range of 10–110° (step size = 0.02° and a counting time = 1 s per step). Some rolled strips, with surfaces parallel to the rolling direction, were cut to 10 mm × 10 mm in size in order that microstructural observations could be performed. To observe the changes in microstructure caused by cold deformation, the samples were prepared according to the conventional metallographic procedures (grinding and polishing) and etched with Nitric-Acetic Etchant (10 ml HNO_3 and 90 ml CH_3COOH for 40 s).

2.3. Electrochemical measurement

Electrochemical experiments were done on the surface of CG and FG pure nickel samples of pure nickel in two borate buffer solutions with different pH value of 9.0 (0.01 M $Na_2B_4O_7$ + 0.01 M H_3BO_3) and 8.5 (0.01 M $Na_2B_4O_7$ + 0.05 M H_3BO_3) at 25 ± 1 °C. Both of boric acid and borax were Merck products and has a purity of 99%. Prior to any test, each sample was grounded with SiC abrasive paper up to 2000 grit, then washed with distilled water and dried by blowing cold air. All experiments were accomplished in a flat cell under aerated condition by the μAutolab Type III/FRA2 system. The pure nickel samples were made as a working electrode (0.63 cm^2 exposure area), a Pt rod was applied as a counter electrode and an Ag/AgCl saturated in 3.0 M KCl was used as a reference electrode. For the curve-fitting method, NOVA 2.1.0 software was used.

Prior to any electrochemical tests, each specimen was immersed in the test solution for 1800s at the open circuit potential (OCP) to form a stable passive layer. The PDP plots were obtained starting from -0.25 V (Vs. E_{corr}) to 1.0 $V_{Ag/AgCl}$ (scan rate = 1 mV/s). Prior to EIS and M–S experiments, Anodic polarization at various anodic potentials (0.2 $V_{Ag/AgCl}$, 0.4 $V_{Ag/AgCl}$, 0.6 $V_{Ag/AgCl}$ and 0.8 $V_{Ag/AgCl}$) was performed for 1800s, in order to generate a steady-state passive layer. Then EIS tests were performed at the OCP condition (frequency range = 100 kHz to 10 mHz and excitation potential = 10 mV). Moreover, M–S analysis was done on the passive layers in the cathodic direction (step potential = 25 mV and frequency = 1 kHz).
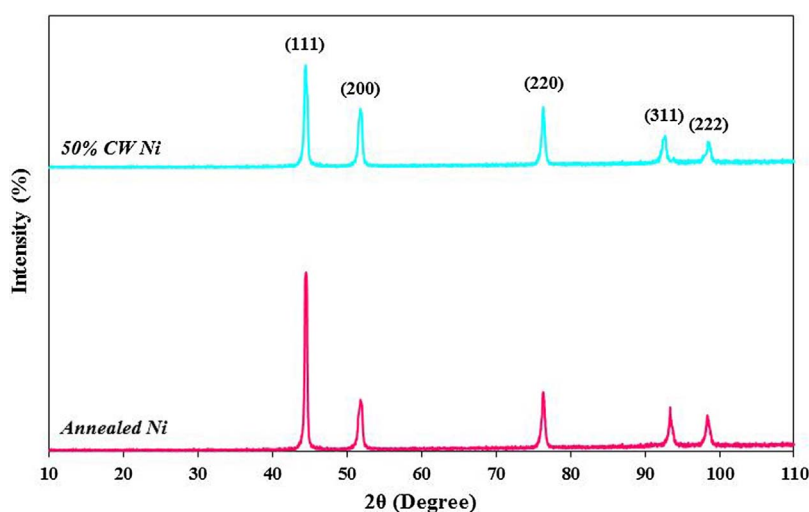
Fig. 1. XRD patterns of CG and FG pure nickel samples.