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Full Length Article

Thermally oxidized Inconel 600 and 690 nickel-based alloys characterizations by combination of global photoelectrochemistry and local near-field microscopy techniques (STM, STS, AFM, SKPFM)

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ABSTRACT

Thermally oxidized nickel-based alloys are studied by scanning tunnelling microscopy (STM), scanning tunnelling spectroscopy (STS), atomic force microscopy (AFM), scanning kelvin probe force microscopy (SKPFM) and photoelectro-chemical techniques as a function of oxidation time at a fixed temperature of 623 K. By photoelectrochemistry measurements we identify the formation of three oxides NiO, Fe_2O_3, Cr_2O_3 and determine the corresponding gap values. We use these values as parameter for imaging the surface at high bias voltage by STM allowing the spatial localization and identification of both NiO, Fe_2O_3 oxide phases using STS measurements. Associated to Kelvin probe measurements we show also that STS allow to distinguished NiO from Cr_2O_3 and confirm that the Cr_2O_3 is not visible at the surface and localized at the oxide/steel interface.

1. Introduction

Due to their lower sensitization to corrosion compared to austenitic stainless steels, nickel-based alloys became an important component material for equipping chemical and nuclear power plants especially steam generators in pressurized water reactors (PWR). The first used nickel-based alloy is the Inconel 600 for its favourable mechanical, chemical and thermal properties such as strength and ductility over a wide range of service temperatures and particularly for its superior corrosion resistance compared to austenitic stainless steels. These latter and traditional materials which have been widely used in the past are susceptible to many corrosive problems especially in high temperature environments. These problems are related to pitting corrosion and transgranular stress corrosion cracking (TGSCC) in chloride-containing solutions [1–9]. However, in some special uses and environments such as tubing material of steam generators for pressurized water reactors (PWRs) even the alloy 600 present corrosive problems like susceptibility to intergranular corrosion (IGC) or intergranular stress corrosion cracking (IGSCC) whose severity depends on microstructural properties [10], environment [11], and use conditions [12]. It has been shown that the susceptibility of alloy 600 to IGSCC can be assigned to grain boundary chromium depletion. Therefore Inconel 690 which contains approximately twice chromium concentration (30 wt.%) than Inconel 600 with similar composition for other elements has been chosen in many applications. The high chromium

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content of Inconel 690 provides high resistance to corrosion in a wide range of aqueous environments and is therefore used in many nuclear and petrochemical steam generators [13]. However, it has been reported that Inconel 690 is still susceptible to IGSCC [4,14] and to pitting corrosion in some caustic aqueous environments containing chloride (Cl^-) and/or thiosulfate ions ($S_2O_3{}^{2-}$) [15]. So, the understanding of the formation mechanisms and properties of the oxide layers of nickel-based alloys remains an important research subject.

Although some papers [16–18] have reported on the properties of oxide layers of Inconel material in different conditions and environments, the detailed exploration of austenitic Ni-Cr-Fe alloys with high nickel content have received less attention than stainless steels. The experimental works on these alloys are performed at high temperature, high pressure water, steam generators and simulation (SG) in the reactors pressurized water reactors (PWR) primary water, both in the dynamic flow conditions or in static autoclaves. Among these studies, pitting corrosion of Inconel type 600 tubes has been conducted in various steam generator environments [19]. It is currently admitted that nucleation and growth of corrosion cracking depends strongly to the protective properties of passive films formed on metal surface [20,21]. Although the studies of oxides and passive films on stainless steels and nickel-based alloys have been investigated [22–28], the relationship between the chemical composition and structure of the films and their protective character is still a matter of considerable debate. Consequently, a considerable number of investigations have been devoted to the study of the structural and electronic properties and chemical compositions of oxide and passive films, particularly on stainless steels and nickel base alloys [28–41]. Experimental results reveal that the formation of a *p-n* junction in the oxide, the repartition of the different oxide phase within the oxide layer and at the steel/oxide interface, the position of Cr_2O_3 which seems to protect the steel when it is situated at the interface are the relevant parameters to control. For example, studies [33,34] carried out with passive films formed on nickel-based alloy 600 in borate buffer solution at pH = 9.2 have demonstrated that these films can be more accurately described as a duplex structure composed of a semiconducting n-type outer region containing mixed iron–nickel oxide and hydroxide and a p-type inner region containing chromium oxide. However, the system formed by the passive film, the metallic substrate and the electrolyte is rather complex and the relationship between the structure, chemical composition and electronic properties of films and their ability to protect the underlying metal or alloy from different types of corrosion is still a matter of considerable debate.

The goal of the present work is to link structural and photoelectrochemical properties of thermally grown oxides on nickel-base alloys (Inconel 600 and 690) and to follow the oxidation process as a function of time in detail. These investigations are performed by local near-field imaging techniques like scanning tunnelling microscopy (STM), scanning tunnelling spectroscopy (STS), atomic force microscopy (AFM), scanning kelvin probe force microscopy (SKPFM) and by the global in situ technique named photoelectrochemistry. We determine the semiconducting properties of nickel based alloys using a model based on the Gärtner description of depletion layer photoeffects in semiconductors [42,43]. We present, to our knowledge, the first determination of the band gap of the outer oxide layer for nickel-based alloys using STS techniques. The gap values measured by STS are compared to that extracted from photoelectrochemical experiments. Afterwards, STM imaging at a potential higher than the band gap allow the localization at the nanometric scale of the several oxides (NiO and Fe_2O_3) presents on the surface. We confirm that the Cr_2O_3 is not visible at the surface and localized at the oxide/steel interface and therefore confirm the model proposed by Marchetti et al. [44]. We compare the appearing roughness in STM with the true roughness of the sample obtained by AFM.

2. Experiments

The composition of the used nickel-based alloys (Inconel type 600 and 690) is presented in Table 1. The samples, of surface area s = 0.8 cm^2 are annealed in an ultra high vacuum experimental setup (basic pressure below 10^{-10} mbar) for 30 min at 1423 K to avoid cracking. Afterwards, they are abraded with wet SiC paper of different grit size, rinsed in distilled water, ultrasonically cleaned and dried with air. Oxidation of the samples was made in air, at a fixed temperature of 623 K in a furnace, for different durations between 1 h and 1176 h (7 weeks) at atmospheric pressure.

For photoelectrochemical measurements, a cell with three electrodes is used with a platinum counter-electrode (area = 1 cm^2) and a saturated calomel electrode (SCE) as reference. All experiments were carried out at room temperature (295 K) under continuous high purity nitrogen bubbling in a buffer solution of composition H_3BO_3 (0.05 M) + $Na_2B_4O_7.10H_2O$ (0.075 M) leading to pH = 9.2. The specimens previously oxidized were immersed in the solution and left at rest potential also called open circuit potential for 2 h before measurements were taken. The photocurrent is generated by focusing the light (150 W xenon lamp) with a fused silica lens through a quartz window of the electrochemical cell onto the working electrode. A lock-in technique with a double phase synchronised detector (Brookdeal 5208 lock-in amplifier) is used to separate the photocurrent from the sample current by chopping the light at a constant frequency (19 Hz) and feeding the signal as well as the current output of the potentiostat (PAR 273). The photocurrent spectra are obtained by scanning the light wavelength in steps of 50 nm from 750 to 250 nm using à 1200/mm grating monochromator (Jobin Yvon H25). The dependence of the photocurrent on the applied potential U is obtained at a fixed wavelength (350 nm) by scanning successively the applied potential in steps of 50 mV in the potential range 1 V/SCE to −1.5 V/SCE. The photocurrent spectra are corrected for the lamp efficiency without taking into account of the reflections at the film-solution interface.

STM and STS measurements were performed using the STM head provided with a commercial AFM (multimode design and nanoscope V electronic from Brucker) that we also use with the AFM head for AFM topography and SKPFM imaging. PtIr coated tapping mode Si tips provided by Bruker with resonant frequency around 75 kHz and stiffness constant around 3 N/m have been used for the AFM and SKPFM images. Our experimental procedure to obtain a SKPFM images has been described in a previous paper [37]. For STM measurements, Pt-Ir tips were cut from a Pt-Ir wire (diameter = 0.3 mm). The potential is applied to the sample connected to a plate using a silver paint and the current flowing across the tip detected and amplified by a pre-amplificator.

Table 1
Composition of the alloy 600 and 690 (wt%).

	C	N	Cr	Fe	Mo	Si	Mn	Ti	P	S	B
600	0.033	0.007	16.30	7.82	–	0.28	0.65	0.28	0.007	0.003	–
690	0.015	0.041	29.00	10.00	–	0.31	0.30	0.31	0.009	0.001	–