

# Corrosion Resistance of the Inconel 740H Nickel Alloy after Pulse Plasma Nitriding at a Frequency of 10 kHz

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The microstructure and corrosion resistance of the CrN, Cr<sub>2</sub>N layer produced by pulse plasma ion nitriding at a frequency of 10 kHz on the Inconel 740H nickel superalloy were examined. The microstructure of the layers were characterized by light microscope and scanning electron microscopy. The corrosion resistance was examined by the impedance and potentiodynamic methods in a 0.1 M Na<sub>2</sub>SO<sub>4</sub> solution and an acidified (pH = 4) 0.1 M NaCl solution at room temperature. The layer obtained, about 4.5 μm thick, contains CrN, Cr<sub>2</sub>N phases. It is continuous on the entire cross-section of the sample and adheres well to the substrate. However, in the chloride environment it constitutes an inhomogeneous cathodic coating for corrosion and thereby intensifies pitting corrosion of the material. In chloride-less environment, on the other hand, the layer has no essential effect on the corrosion rate of the Inconel 740H nickel alloy.

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## 1. Introduction

Nitride layers show high hardness and good resistance to frictional wear and corrosion. They can be successfully produced on e.g. austenitic and ferritic steels by the surface engineering methods [1–3]. The use of glow-discharge assisted nitriding for treating nickel superalloys is much rarely reported in the literature [4]. Most of the reported studies are concerned with steel, whereas the nitride layers obtained on nickel alloys by this technique conducted under the same or similar conditions are thinner and may degrade the corrosion resistance of the alloy [5, 6].

In the present study we were concerned with the Inconel 740H nickel alloy subjected to glow-discharge assisted plasma nitriding at a frequency of 10 kHz conducted at a temperature of 570 °C for 8 h, and the aim was to examine the structure of the nitride layer being formed on the alloy surface and the corrosion resistance of the thus-treated alloy (measured in the 0.1 M Na<sub>2</sub>SO<sub>4</sub> and 0.1 M NaCl (pH = 4) solutions at room temperature.

## 2. Examination methods

The materials examined were the Inconel 740H (nickel-chromium-cobalt) nickel alloy in the initial state and this alloy after subjecting it to ion nitriding at a frequency of 10 kHz at a temperature of 570 °C for 8 h.

The corrosion resistance was examined in two corrosive solutions, namely, 0.1 M Na<sub>2</sub>SO<sub>4</sub> and acidified (pH = 4) 0.1 M NaCl, at room temperature, by the impedance and potentiostatic methods using an AutoLab POSTAT 100 potentiostat.

The impedance examinations were conducted in a three-electrode system (tested sample-saturated calomel electrode SCE-auxiliary platinum electrode) within the frequency range from 10<sup>5</sup> to 10<sup>-3</sup> Hz at the sinusoidal signal amplitude of 20 mV. The impedance spectra were plotted in the form of the Bode diagrams and analyzed using the Baukamp EQUIVCRT software. The potentiodynamic examinations were conducted in the same three-electrode system within the potential range from -400 to +1500 mV. The polarization potential rate was 0.2 mV/s.

## 3. Results

Figure 1 shows a cross-section of the layer produced on Inconel 740H by glow-discharge assisted nitriding. The thickness of the layer was evaluated at about 4.5 μm. The layer was homogeneous and continuous on the entire cross-section of the sample. The X-ray phase analysis performed within the angle range from 20 to 120° shows that the layer is composed of two phases, namely CrN, Cr<sub>2</sub>N. The impedance spectra obtained for IN 740H were analyzed using equivalent circuits (EC).

Figure 2a represents the EC for the two-time constants model R(RQ)(RQ) used for a solution of Na<sub>2</sub>SO<sub>4</sub> whereas R(Q[R(RQ)]) was used for environments chloride (NaCl + H).

Figure 3 shows the impedance spectra obtained for Inconel 740H alloy exposed in the two mentioned above corrosive environments before and after the ion nitriding.

In the case of the initial state exposed in 0.1 M Na<sub>2</sub>SO<sub>4</sub> (Fig. 3a) we can suppose that the two capacitance peaks represent two metallic phases. From the fact that the values of the parameters *n* of these two phases are similar (0.89 and 0.87) we can infer that both phases are in the passive state with high corrosion resistance. Based on the literature data we can assume that the phases present on the surface of the Inconel 740H alloy can be identified as aluminum oxides and chromium oxides. The ion

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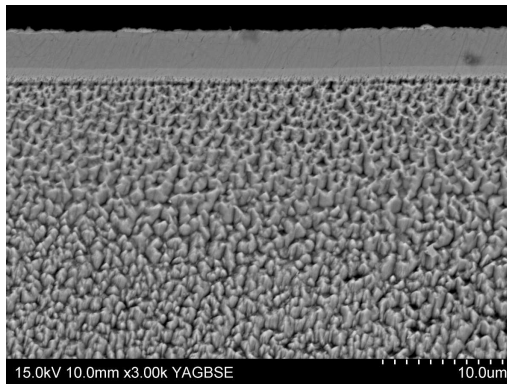


Fig. 1. Microstructure of the layer produced on the Inconel 740H nickel alloy by glow-discharge assisted nitriding at a temperature of 570 °C for 8 h.

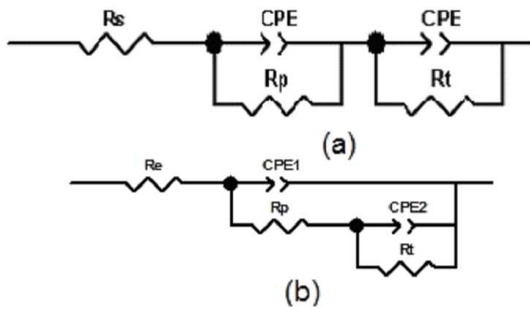


Fig. 2. Equivalent circuits: (a) R(RQ)(RQ) Na<sub>2</sub>SO<sub>4</sub>, (b) R(Q[R(RQ)]) NaCl+H. CPE — constants phase element,  $R_s$  — resistance of the solution,  $R_p$  — resistance of the roughness layer,  $R_t$  — charge transfer resistance through the double layer.

nitriding treatment applied to the alloy altered significantly the electrochemical homogeneity of the substrate. The presence of the maximum of the capacitance loop at high frequencies indicates that the substrate is liable to local corrosion. However, the data given in Table I show that the corrosion resistance of the material has only been slightly lowered. This can be inferred from the changes of the resistance  $R_t$  (from  $5.8 \times 10^5 \Omega \text{ cm}^2$  (initial state) to  $2.6 \times 10^5 \Omega \text{ cm}^2$  (nitrided)) with the capacitance of the layer being almost unchanged. It is only the significant decrease of the parameter  $n$  (from 0.87 to 0.79) which indicates that the durability of the layer exposed in sulphate solutions has been considerably shortened.

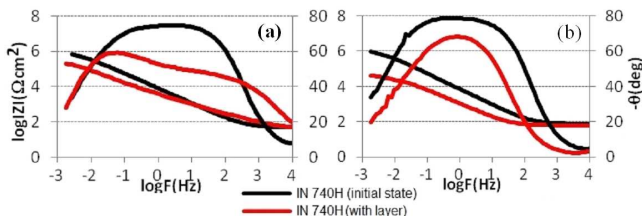


Fig. 3. Impedance spectra of the nitrided layers exposed in (a) 0.1 M Na<sub>2</sub>SO<sub>4</sub> and (b) 0.1 M NaCl (pH = 4).

The spectra obtained for the initial state exposed in the acidified chloride solution (0.1 M NaCl+H) contain two capacitance peaks with different parameters  $n$  (0.81 and 0.96) which indicates presence of two phases whose electrochemical activities differ significantly (Fig. 3b). It can be supposed that the regions with higher electrochemical activity are phases enriched with aluminum atoms which are active when exposed in the environment with  $\text{pH} \leq 4$ . During the ion nitriding, the corrosion resistance of the substrate was degraded which we can see from the decreased values of the resistance  $R_t$  (from  $7.35 \times 10^5$  to  $2.52 \times 10^4 \Omega \text{ cm}^2$ ) and the decreased parameter  $n$ . The relatively low values of the parameter  $n$  observed in the nitrided layer indicate that the substrate was actively dissolved due to the lowered pH and also to the presence of local regions in which the electrochemical activity of the processes is decided by the diffusion phenomena. All these results are typical of intensive pitting corrosion.

TABLE I

Characteristic electrochemical parameters of the nitrided layers (impedance method).

			$R_s$	$R_p$	$R_t$
Na <sub>2</sub> SO <sub>4</sub>	IN 740H (initial state)	$R [\Omega \text{ cm}^2]$	45	$1.03 \times 10^4$	$5.80 \times 10^5$
		$C [\text{F}/\text{cm}^2 \text{ s}^{n-1}]$		$1.51 \times 10^{-4}$	$2.38 \times 10^{-5}$
		$n$		0.85	0.89
	IN 740H with layer	$R [\Omega \text{ cm}^2]$	32	$4.18 \times 10^3$	$2.61 \times 10^5$
	$C [\text{F}/\text{cm}^2 \text{ s}^{n-1}]$		$1.43 \times 10^{-4}$	$9.75 \times 10^{-5}$	
	$n$		0.52	0.79	
NaCl+H	IN 740H (initial state)	$R [\Omega \text{ cm}^2]$	76	$1.39 \times 10^5$	$7.35 \times 10^5$
		$C [\text{F}/\text{cm}^2 \text{ s}^{n-1}]$		$6.25 \times 10^{-5}$	$4.25 \times 10^{-5}$
		$n$		0.81	0.96
	IN 740H with layer	$R [\Omega \text{ cm}^2]$	60	$2.75 \times 10^4$	$2.52 \times 10^4$
	$C [\text{F}/\text{cm}^2 \text{ s}^{n-1}]$		$2.0 \times 10^{-4}$	$4.23 \times 10^{-4}$	
	$n$		0.81	0.69	

The results of potentiodynamic examinations (Fig. 4) confirm that the nitriding process has a negative influence on the corrosion resistance of the Inconel 740H alloy.

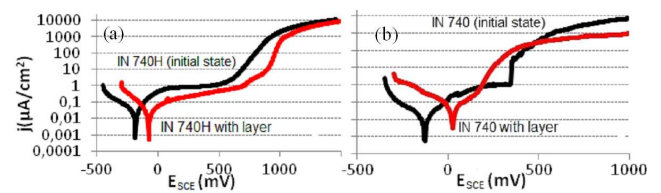


Fig. 4. Potentiodynamic curves obtained for the Inconel 740H alloy exposed in (a) 0.1 M Na<sub>2</sub>SO<sub>4</sub> and (b) 0.1 M NaCl+H in the initial state and after nitriding process.

It can be seen that, in the chloride-less solution (Fig. 4a), the materials are in the passive state within a wide range of potentials. The increased current density observed in the untreated material above a potential of +600 mV can be associated with the presence of

the trans-passive region and changes in the oxidation degree of the chromium compounds. Above +1000 mV, the substrate undergoes uniform corrosion dependent on the diffusion currents at the interface. The shift of the corrosion potential towards anodic potentials observed in the nitrated CrN, Cr<sub>2</sub>N layer indicates that the layer has a cathodic character. The increased nobility of the substrate results in a decrease of the current density in the passive region but may promote pitting corrosion especially in chloride environments. An analysis of the potentiodynamic curve obtained for the nitrated layer shows that the material is in the passive state within a wide range of potentials. The increase of the polarization potential to above 750 mV initiates intensive degradation of the nitrated layer and its spalling. The values of the current density given in Table II indicate that the ion nitriding has not degraded the high corrosion resistance of the initial state. Figure 5 shows the corrosive damage of the nitrated layers after the potentiodynamic examinations conducted in the chloride-less solution.

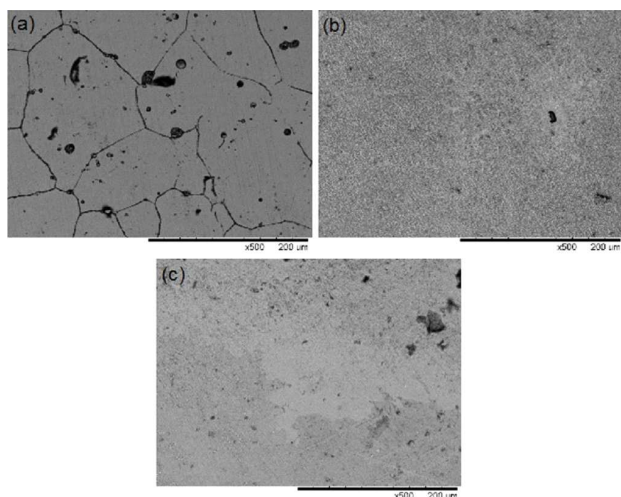


Fig. 5. Corrosion damage of the Inconel 740H alloy after corrosion tests conducted in the Na<sub>2</sub>SO<sub>4</sub> solution (a) in the initial state, (b) spalling of the nitrated layer, (c) corrosion of the nitrated layer below its surface zone.

It can be seen from Fig. 5a that, in the untreated material, the corrosion processes chiefly proceed on the grain boundaries and substantial amounts of carbide precipitates occur within the austenite grains. Figure 5b and c shows the nitrated layer with visible surface spalling. The ion nitriding process resulted in increased twinning of the austenite grains, which undoubtedly contribute to an increase of the microhardness and creep resistance of the material.

The results of the corrosion test conducted in the acidified chloride solution indicate that the substrate is susceptible to pitting corrosion. In the untreated material, the wide passive range in the anodic region and the low passive current densities ( $i_p = 1 \mu\text{A}/\text{cm}^2$ ) are observed. After the breakdown potential ( $E_{\text{pit}} = 310 \text{ mV}$ ),

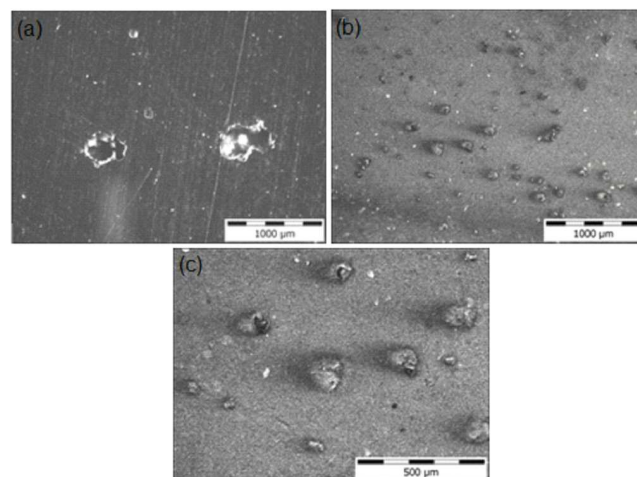


Fig. 6. Corrosion damage of the Inconel 740H alloy after the potentiodynamic examinations conducted in the acidified NaCl solution: (a) in the initial state, (b) and (c) pitting corrosion of the nitrated layer.

intensive pitting corrosion appears (Table II, Fig. 6a). The nitrated layers decrease the corrosion resistance of the substrate, which can be seen from the increase of the corrosion current density (from 0.02 to 0.068  $\mu\text{A}/\text{cm}^2$ ) and the shortening of the durability of the passive layer ( $E_{\text{pit}} = 130 \text{ mV}$ ). The structural defects (Fig. 6b and c) favor the nucleation of corrosion pits.

TABLE II

Characteristic electrochemical parameters of the nitride layer (potentiodynamic examinations).

		$i_{\text{corr}}$ [ $\mu\text{A}/\text{cm}^2$ ]	$i_p$ [ $\mu\text{A}/\text{cm}^2$ ]	$E_{\text{corr}}$ [mV]	$E_{\text{pit}}$ [mV]
Na <sub>2</sub> SO <sub>4</sub>	IN 740H (initial state)	0.028	1	-190	
	IN 740H with layer	0.025	1	-75	
NaCl+H	IN 740H (initial state)	0.02	1	-130	310
	IN 740H with layer	0.068	0.2	+30	130

#### 4. Conclusions

The glow-discharge assisted nitriding conducted in plasma pulsed at a frequency of 10 kHz in a hydrogen–nitrogen atmosphere (75–25 vol.%) at a temperature of 570 °C for 8 h applied to the IN 740H nickel alloy yields a diffusive CrN, Cr<sub>2</sub>N layer about 4.5  $\mu\text{m}$  thick on the alloy surface. The layer functions as an inhomogeneous cathodic coating which, in chloride environments, intensifies pitting corrosion of the material. In chloride-less environments, the nitride layer does not affect substantially the rate of the alloy corrosion.

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