

Surface modification of Ni-Ti alloy by low-temperature nitriding process

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Abstract. In order to create new applications and enhance the performance of NiTi alloys, surface modifications are important to improve their biocompatibility. TiN coatings, due to its low chemical reactivity, high hardness and resistance to wear and corrosion, have been adopted for protecting surface of the NiTi alloys. In presented work the structure of layers formed at surface of the NiTi alloy was reported. The layers were formed using glow discharge technique at low temperature: 300 - 400°C. Thickness, surface roughness, interface roughness, density were calculated using reflectivity measurement. The X-ray grazing diffraction was applied for phase analysis. The chemical composition was determined using the XPS method. Corrosion resistance was studied applying the potentiodynamical method. Electrochemical characteristics of the samples were measured at the room temperature in Tyrod's solution. Results have shown that low temperature nitriding produced the layers, which consisted from the nanocrystalline TiN phase. Relatively high values of corrosion and breakdown potentials proved that the TiN layers as well as the intermediate Ti₃Ni phase effectively protect surface of the NiTi alloys against nickel ion release.

1. Introduction

NiTi alloy has been widely used in biomedical fields due to its special shape memory effect, superelasticity and good biocompatibility. It is an excellent biomaterial for orthopedics, dental application, vascular and organ surgeries [1, 2]. However, these applications, especially as a long term implants, require special attention to respect of nickel ion release into the patient's metabolism and the surrounding tissue. If nickel concentration exceeds a certain level it can cause a toxic effect on the cell or allergy especially in case when patient is highly sensitive [3]. In order to improve the corrosion resistance of the NiTi alloy and suppress the release of nickel ions, various surface modification techniques have been proposed. Titanium oxide [4-6], titanium nitride [7,8] diamond-like carbon (DLC) [9] or alumina [10] has been found as a good candidate for layers, which sufficiently protect human body [11,12]. Additionally, combination of layer sequence, forming the titanium oxide and titanium nitride layers, increases corrosion resistance and biocompatibility [5,7,13]. The titanium oxide, especially TiO₂ [14], increases the stability of the surface layer, creates the physical and chemical barrier against oxygen migration to the top of the surface and limits the way of the nickel oxidation [15]. Low chemical reactivity, high hardness as well as wear and corrosion resistance are characteristic properties of the titanium nitride layers. Reported results show that layers were thick. Moreover, between the layer and the NiTi matrix a sublayer of intermetallic phases such as Ni₃Ti or Ti₂Ni were formed [8,13]. Both phases reveal a low plastic property, which limits their practical application in fields of medicine where the shape memory effect or superelasticity is required. Therefore, in the literature still exists discussion concerning improvement of surface biocompatibility in the NiTi alloy.

The present work summarizes results obtained from studies carried out for the nitride layers, which were used for covering surface of the NiTi alloy. The layers were formed using glow discharge technique at low temperature, which did not change the structure of the NiTi.

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2. Experimental procedure

The nitride-oxide layers were deposited on commercial NiTi alloy with nominal chemical composition: 50.6 at.% Ni. Such composition with a combination of quenching, from 800°C to the iced water, ensures that the A_f temperature equals to 10°C. It means that alloy reveals the B2 structure at room temperature. Moreover, the alloy revealed superelastic properties. Rectangular samples of the alloy with dimension of 14 x 12 x 0.8 mm were mechanically polished using SiC papers down to 1200 grid. Next diamond suspensions were used and final treatment of the surface was done using 0.1 μm colloidal silica suspension. The layers were formed using glow discharge technique at low temperature (300°C, 350°C or 400°C) applying various time and atmosphere conditions.

Structure of obtained surface was examined applying the X'Pert Pro (Philips) diffractometer (40 kV, 30 mA, Cu $K_{\alpha 1}$ and α_2 radiation). First, phase analysis was done using the X-ray grazing diffraction technique (GIXD). The X-ray diffraction patterns were measured in the range of 2θ between 20° and 80° using grazing incidence angle of $0,10 \div 0,80^\circ$. Next, thickness, surface roughness, interface roughness, density were calculated from reflectivity measurement. Detailed microstructural analysis and observations were carried out on a cross-section specimens using a transmission electron microscope JEM-3010 (JEOL) equipped with an electron spectroscopy detector (EDS). Accelerating voltage was 300kV. The XPS method was used for chemical and electron structure analysis.

The transformation temperatures of the nitrided NiTi alloy were determined from the DSC cooling/heating curves registered using a Perkin-Elmer instrument.

The corrosion resistance of the coated alloy was tested at room temperature in the physiological Tyrod's solution using the cyclic potentiodynamic polarization method (VoltaLabTM2). After the polarization test, the sample surface was studied using scanning electron microscopy JSM-6480 (JEOL)

3. Results and discussion

The information about the structure of the layers, formed on NiTi alloy, was obtained from analysis of the X-ray grazing diffraction patterns. Decrease of the penetration depth of the X-ray beam, which is realised by decrease of incidence angle, allows receiving diffraction pattern from the top of the surface. The X-ray

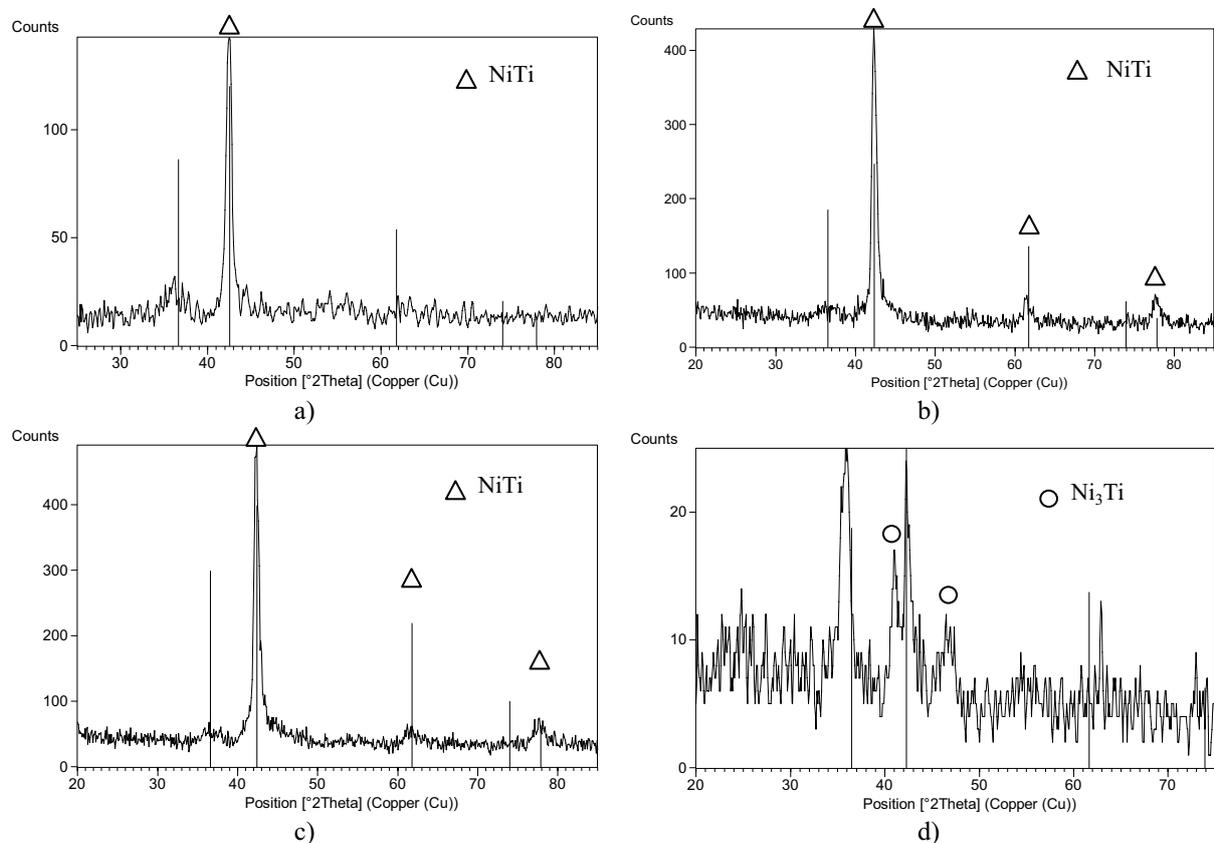


Fig. 1 The X-ray diffraction patterns obtained at constant incidence angle of: a) – 0,15°, b) – 0,25°, c, d) – 0,30° for surface layer formed at: a) – 350°C/10min, b) - 300°C/1h, c) - 300°C/1h, cooling in H₂, d) - 400°C/5min

diffraction patterns, which were registered using incidence angle higher than $0,5^\circ$ revealed a presence of strong 110 peak, which belongs to the B2 phase – matrix of NiTi alloy. Decrease of the incidence angle caused increase of the volume fraction of the TiN phase which formed the layer. In results of this the peaks characteristic for the TiN phase showed higher intensity and were distinguishable from the background (Fig. 1). The bars shown in diffraction patterns mark an angular position of the diffraction lines belonged to the TiN phase. Very weak and wide peak of the TiN phase were observed in diffraction pattern obtained at grazing angle $0,15^\circ$ for the nitrided layer formed at 350°C for 10 minutes (Fig 1a). It means that this layer is very thin and could possess amorphous or nanocrystalline structure. Increase of the processing temperature up to 400°C caused increase of the thickness of the TiN layer (Fig. 1d) – in diffraction pattern taken at constant incidence angle of 0.3° only diffraction lines characteristic for the TiN phase and the Ni_3Ti phase were identified. It proves that between nitride layer and the NiTi matrix a sublayer formed from the Ni_3Ti phase is created. Formation of this phase under nitride layer shows that the temperature of the process was too low and time too short to create the sublayer of equilibrium Ti_2Ni phase [7, 8]. However, presence of the Ni_3Ti intermediate layer decreased the quality of the nitriding process, when these processing parameters are used. The presence of Ni_3Ti phase was not stated from diffraction patterns obtained for the layers formed at lower temperatures and at time up to 1 hour (Fig. 1b,c). The calculated half-width of the 111_{TiN} diffraction peak – 1.2° proves that layer possesses nanocrystalline structure with average crystallite size of 9,2 nm.

The detailed information concerning the parameters of the layers formed on NiTi alloy using glow discharge technique at low temperature were calculated from reflectivity curves. Figure 2 shows the set of the measured curves. The shape of the curves obtained for nitride layers produced at 300°C , 350°C after 10min deposition are characteristic for the very thin layers. The parameters of the layers such as thickness, surface roughness and density determined from reflectivity curves are compared in table 1.

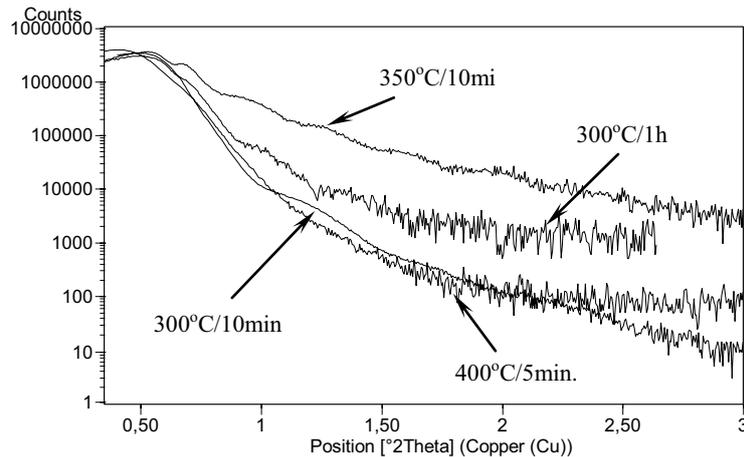


Fig. 2 The experimental reflectivity curves measured for the sample nitrided at $300^\circ\text{C}/10\text{min}$ (a), $350^\circ\text{C}/10\text{min}$ (b), $300^\circ\text{C}/1\text{h}$ (c) and $400^\circ\text{C}/5\text{min}$ (d) NiTi samples

Table 1. The structural characteristic of the nitrided NiTi alloy obtained from the X-ray grazing diffraction (GIXD) and the reflectivity (XRR) measurements

Parameters of the nitriding process	Phase	Thickness [nm]	Surface roughness [nm]	Density [g cm^{-3}]
$300^\circ\text{C}/10\text{min}$	NiTi	-	0,81	5,86
	TiN	6,22	4,1	5,08
$300^\circ\text{C}/1\text{h}$	NiTi	-	7,6	5,91
	TiN	47,4	2,4	4,46
$300^\circ\text{C}/1\text{h}$, cooling in H_2	NiTi	-	26,4	6,08
	TiN	64,6	9,5	4,63
$350^\circ\text{C}/10\text{min}$	NiTi	-	1,55	5,25
	TiN	23,1	1,19	4,65
	TiO_2	0,26	0,96	2,52
$400^\circ\text{C}/5\text{min}$	NiTi	-	1,3	5,96
	Ni_3Ti	35,2	9,2	4,49
	TiN	62,5	1,7	5,05

Obtained parameters show that the layer formed during nitriding for short time at 350 °C is about 23 nm thick and characterizes which low roughness of the surface and interface between the TiN layer and the NiTi matrix. The TiN layer formed at 300°C possesses relatively high roughness of the surface, when compare to the total thickness of the layer, and calculated density of the TiNi phase is much lower than one determined for the bulk alloy. It means that the TiN layer was not fully formed and high amount of pores or irregularities at the interface can be finding. Results obtained for the TiN layer formed using the nitriding temperature at 400 °C for 5 minutes are comparable to that obtained for the processing at 300°C/1h cooled in H₂. However, presence of sublayer formed from the Ni₃Ti phase in process carried out at 400°C/5min. eliminates this material for practical applications. It is worthy to notice that at the top of the TiN layer the titanium oxide was formed. Thickness of the TiO₂ was about 0.3nm.

The transmission electron microscopy observation confirmed the results obtained from X-ray diffraction studies carried out for the layer obtained at 400°C/5min applying glow discharge technique (Fig. 3). Observation carried out on the cross-section of the layers reveals the structure of the TiN layer and intermediate layer of the Ni₃Ti phase. The determined average thickness of these layers is 68 nm and 39 nm, respectively. Both values are comparable to that determined using reflectivity measurements (Table 1). The top of the TiN layer reveals low roughness of the surface. Higher roughness can be seen at surfaces between the Ni₃Ti interlayer and the TiN layer as well as the NiTi matrix. Moreover, the electron microscopy proved nanocrystalline structure of nitride layer. The average size of the TiN nanograins was about 10 nm. Figure 3b shows selected area diffraction pattern taken from the TiN layer. It can be seen that background of polycrystalline rings, which come from TiN phase, is broaden and characteristic for an amorphous phase. It can be concluded that the part of the TiN layer is amorphous.

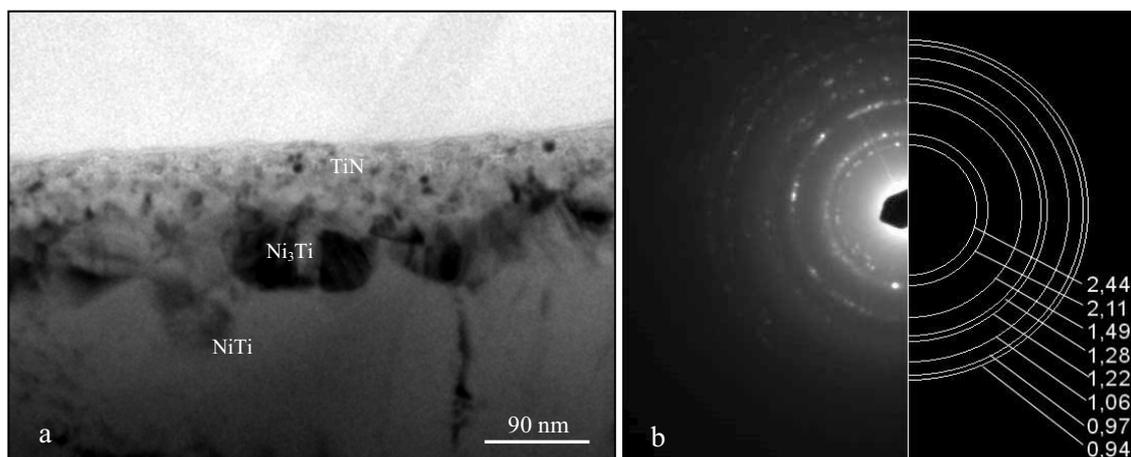


Fig. 3 Microstructure of the cross-section of the layer, which was obtained at 400°C for 5min (a), selected area diffraction pattern from TiN layer (b)

The chemical composition of the layer after nitriding at 350°C for 10 min was investigated using X-ray photoelectron spectroscopy (Fig. 4). Particular analysis of the Ti 2p XPS spectra proved, that formed during nitriding process layer consists of the TiN phase and small amount of TiO₂. The presence of TiO₂ in nitride layer was also stated from the modelling of the reflectivity curve. The analysis of the N 1s spectra (Fig. 4a) shows that titanium nitride dominates at the top of the formed layer. Changes of intensity of peaks of N 1s XPS spectra results in formation of such compounds as N₂, N-C and NO_x. The quantity of these compounds decreased with the depth of layer. The XPS investigation shows that the top of the layer, practically, is free from the nickel atoms.

The potentiodynamic studies carried out in the physiological Tyrod's solution at room temperature using the cyclic potentiodynamic polarization method indicated good corrosion resistance of the nitrided NiTi alloy. The corrosion parameters of the NiTi alloys are summarized in Table 2. The comparison of these parameters shows that the best corrosion resistance revealed the layer which has the highest thickness i.e. formed at 400°C. In this case the potential of corrosion was -80 mV. From the other site, the best values for the breakdown potential and current density was obtained for layers deposited at 350°C for 10 min. (Fig. 5).

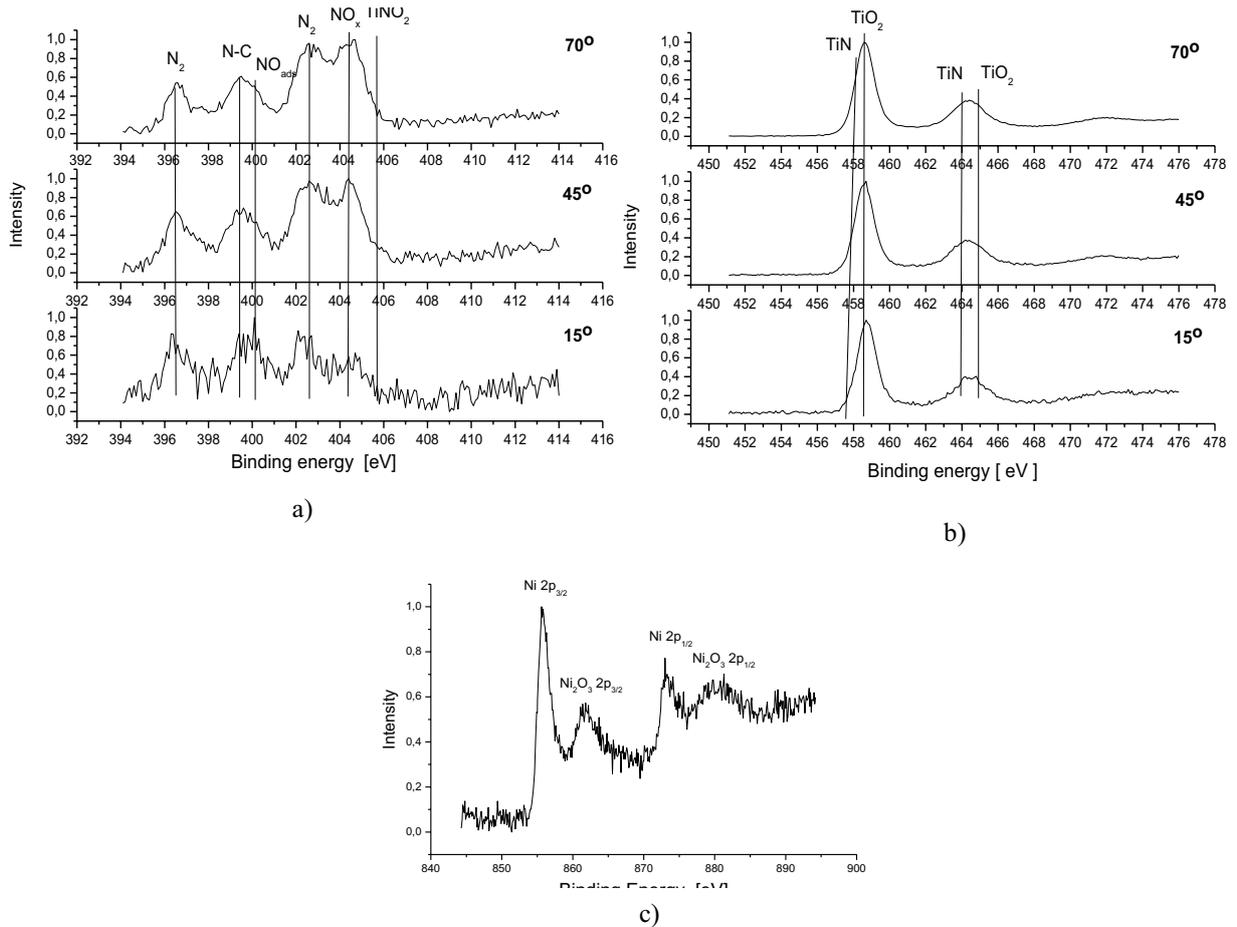


Fig. 4 The photoelectron spectra of 1s nitrogen (a), 2p titanium (b) and 2p nickel (c) for different detection angles of a specimen nitrated at 350°C for 10 min

Table 2. The corrosion resistance of the nitrated/oxidized NiTi alloy measured in the Tyrod's solution using the cyclic potentiodynamic polarization method

Parameters of the nitrating process	E _{corr.} [mV]	E _{br} [V]	j _{br.} [mA cm ⁻²]
300°C/ 10min	- 365	2,39	7,48
300°C/ 1h	- 455	2.41	12.29
300°C/ 1h, cooling in H ₂	- 394	2,36	13,48
350°C/ 10min	- 321	3.24	37.1
400°C/ 5 min	- 80	2,1	-

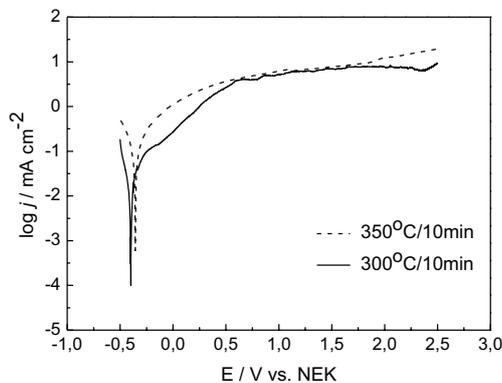


Fig. 5 Electrochemical corrosion test for nitrated NiTi alloy carried out in Tyrod's solution

Based on the received results for studied samples, it may be summarized that glow discharge technique at low temperature appeared as a process for improving properties of the NiTi alloys when they are expected to be used as a biomaterial. The layers formed on NiTi alloy using processes at temperature range 300°C – 400°C differ in thickness, structure and corrosion resistance. The layer obtained at 400°C revealed high potential of corrosion comparable to that obtained after passivation of the NiTi alloys [5]. These properties appear mainly from high thickness of the TiN layer. Disadvantage of the sample nitride at 400°C is its structure. The presence of thick sublayer consisted of the Ni₃Ti phase is unprofitable for biomedical applications. Good quality of nitride layer comes from the nanocrystalline grains of TiN phase. From this point of view more promising is the nitride layer obtained at 350°C for 10 min. Low thickness and absence of Ni₃Ti sublayer as well as high corrosion resistance are main properties which promoted its application for surface protection of NiTi alloys.

4. Conclusions

The glow discharge technique at low temperature is a feasible process for improving the corrosion resistance of NiTi alloy for medical application.

The nitriding process carried out at temperature range of 300°C – 350°C for 10 min. formed thin layer which only consists from nanocrystalline TiN phase.

The nitriding at 350°C for 10 min. is the preferred process to form nitride layer on NiTi alloy for medical implants using shape memory effect. The thickness of this TiN surface layer is about 23 nm and it is characterised with high corrosion resistance - potential corrosion $E_{\text{corr}} = -321$ mV and breakdown potential $E_{\text{br}} = 3.24$ V.

The best corrosion resistance was obtained for the layer obtained at 400°C. In this case the potential of corrosion is $E_{\text{corr}} = -80$ mV and is close to the layer after passivation. The problem of this surface is presence of sublayer of Ni₃Ti phase between TiN top layer and NiTi matrix.

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