

EFFECT OF DIFFUSE NITROGEN SATURATION ON THE STRUCTURE AND MICROHARDNESS OF THE SURFACE LAYER OF Zr-1Nb

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The effect of surface modification with nitrogen from a controlled gas environment on the structure and microhardness of Zr-1Nb alloy has been studied. The database obtained from the results of the durometric and metallographic studies of the surface layers of the Zr-1Nb alloy after nitrogen saturation is important for the quality control of the products in terms of surface microhardness and microstructure of the gradient surface layer as a function of the treatment parameters (time, temperature and pressure of the saturating medium) and also for achieving their optimum hardening to guarantee excellent functionality.

INTRODUCTION

An important place in nuclear power engineering and the nuclear industry is occupied by the problem of creating and improving structural materials, optimizing the structure and increasing operational properties. Structural materials of the active zone of nuclear reactors include, first of all, zirconium alloys [1–4].

The interaction of zirconium products with the operative environment can significantly worsen the physico-mechanical properties of both the surface layer and the product as a whole, which leads to a reduction in their service life [5–8]. To mitigate the adverse effects of the environment, intensive research is underway to develop methods of applying protective coatings or surface modifications to zirconium materials [9–15].

A promising method for the targeted modification of the surface layer of metals and its alloys is thermochemical treatment, in particular the method of thermal diffusion saturation of surface layers with interstitial elements (oxygen and nitrogen) [16–18]. This method has been shown to be effective in improving the properties of titanium and its alloys [19]. Zirconium alloys are similar in structure and properties to titanium alloys, and tests on them have shown a significant increase in durability under cyclic static loading [20–22]. However, there is little data on the effect of surface modification of zirconium alloy layers with interstitial elements by diffusion saturation from a

gaseous environment, so this issue needs to be investigated [23–25].

MATERIALS, SAMPLES AND RESEARCH METHODS

The Zr-1Nb zirconium alloy (Zr ~ 98.97 wt.%, Nb ~ 1.03 wt.%) was chosen as the material for the studies. Diffuse saturation with nitrogen ($P_{N_2} = 10^5$ Pa) was performed over a wide range of temperatures (550; 650; 750; 850, and 950°C) and exposure times (1; 5, and 10 h).

Metallographic studies of Zr-1Nb samples before and after surface modification with nitrogen were carried out using the Epiquant optical microscope. The structure of the alloys after different CTO modes was revealed by a chemical reagent, vol. %: 1 HF + 1 H₂NO₃ + 3 glycerol.

The phase composition of the surface layers was determined by X-ray diffraction analysis on a DRON-3.0 diffractometer in monochromatic Cu K α radiation with focusing according to the Bragg-Brentano scheme.

RESULTS AND DISCUSSION

Based on the durometric and profilometric analyses, the surface microhardness and roughness of the nitrided Zr-1Nb after nitriding were determined (Table 1). According to the results obtained, as the time-temperature parameters of the nitriding regime increased, the surface microhardness, roughness and depth of the modified layer increased.

Table 1

Characteristics of the surface layer of nitrided samples from Zr-1Nb alloy

Nitriding temperature T , °C	Microhardness $HV_{0.49}$, surface roughness R_a , size of modified layer l	Duration of nitriding, h		
		1	5	10
550	$HV_{0.49}$	215±10	220±10	245±25
	R_a , μm	0.061	0.047	0.044
	l , μm	0...2	4...6	10...13
650	$HV_{0.49}$	250±10	350±15	435±15
	R_a , μm	0.049	0.080	0.125
	l , μm	4...6	7...11	16...20
750	$HV_{0.49}$	450±45	720±70	970±50
	R_a , μm	0.327	0.535	0.582
	l , μm	13...17	38...42	53...58
850	$HV_{0.49}$	1015±60	1155±60	1300±70
	R_a , μm	0.595	0.603	0.656
	l , μm	47...53	62...67	100...110
950	$HV_{0.49}$	1670±100	1743±80	1635±100
	R_a , μm	0.387	0.483	0.745
	l , μm	210...220	550...570	630...660

This is explained by the fact that the higher the time-temperature regime, the higher the reactivity and diffusion mobility of nitrogen in the zirconium alloy.

The crystal lattice parameters of the different phases of the zirconium alloy Zr-1Nb also undergo changes after nitriding (Table 2).

Table 2

Crystal lattice parameters of the phases of the nitrided Zr-1Nb alloy

Treatment	Duration of nitriding, h	Phases					
		α -Zr		Zr_2N			ZrN
		a , nm	c , nm	a , nm	b , nm	c , nm	a , nm
Etalon	–	0.3203	0.5147	0.5634	0.5230	0.3253	0.4577
Without treatment	–	0.3213	0.5126	–	–	–	–
550 °C	1	0.3229	0.5141	0.5643	0.5033	0.3269	0.4623
	5	0.3228	0.5143	–	–	–	0.4606
	10	0.3230	0.5147	–	–	–	0.4612
650 °C	1	0.3226	0.5140	0.5546	0.5059	0.3366	0.4594
	5	0.3229	0.5147	0.5636	0.5142	0.3296	0.4601
	10	0.3229	0.5148	0.5634	0.5167	0.3293	0.4596
750 °C	1	0.3261	0.5164	–	–	–	0.4558
	5	0.3270	0.5205	0.5612	0.5142	0.3299	0.4577
	10	0.3272	0.5254	0.5622	0.5149	0.3298	0.4576
850 °C	1	0.3265	0.5227	0.5602	0.5205	0.3271	0.458
	5	0.3275	0.5246	0.5603	0.5214	0.3271	0.4580
	10	0.3272	0.5202	0.5604	0.5192	0.3317	0.4581
950 °C	1	0.3274	0.5244	0.5664	0.5221	0.3278	0.4593
	5	0.3272	0.5253	0.5525	0.5073	0.3300	0.4578
	10	0.3270	0.5260	0.5525	0.5072	0.3301	0.4583

Analysis of the diffraction patterns of nitrided Zr-1Nb shown that as the time-temperature saturation regime increases, the intensity of the α -Zr reflections decreases and at the same time the intensity of the ZrN and Zr_2N reflections increases on the other (Fig. 1). This is probably due to the increase in thickness of the ZrN

and Zr_2N nitride layer, which increases its shielding effect for the α -Zr sub-layer.

Changes in the microstructure of the Zr-1Nb surface layer after nitriding were observed (Fig. 2). As the time-temperature regime of the nitriding was increased, the compound nitride layer became thicker and the matrix grains coarser.

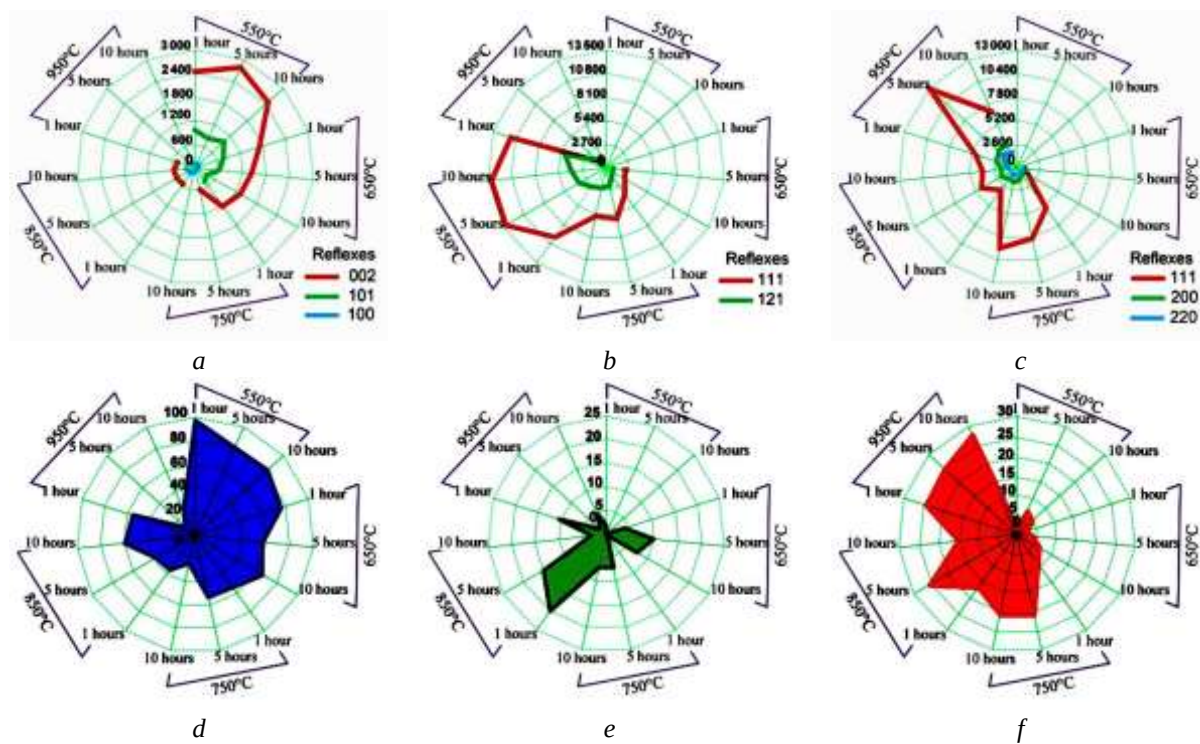


Fig. 1. Intensity and volume of the phases formed on the surface of the Zr-1Nb alloy after nitriding under different regimes: a, b, c – reflex intensity; d – volume α -Zr; e – Zr_2N volume; f – ZrN volume

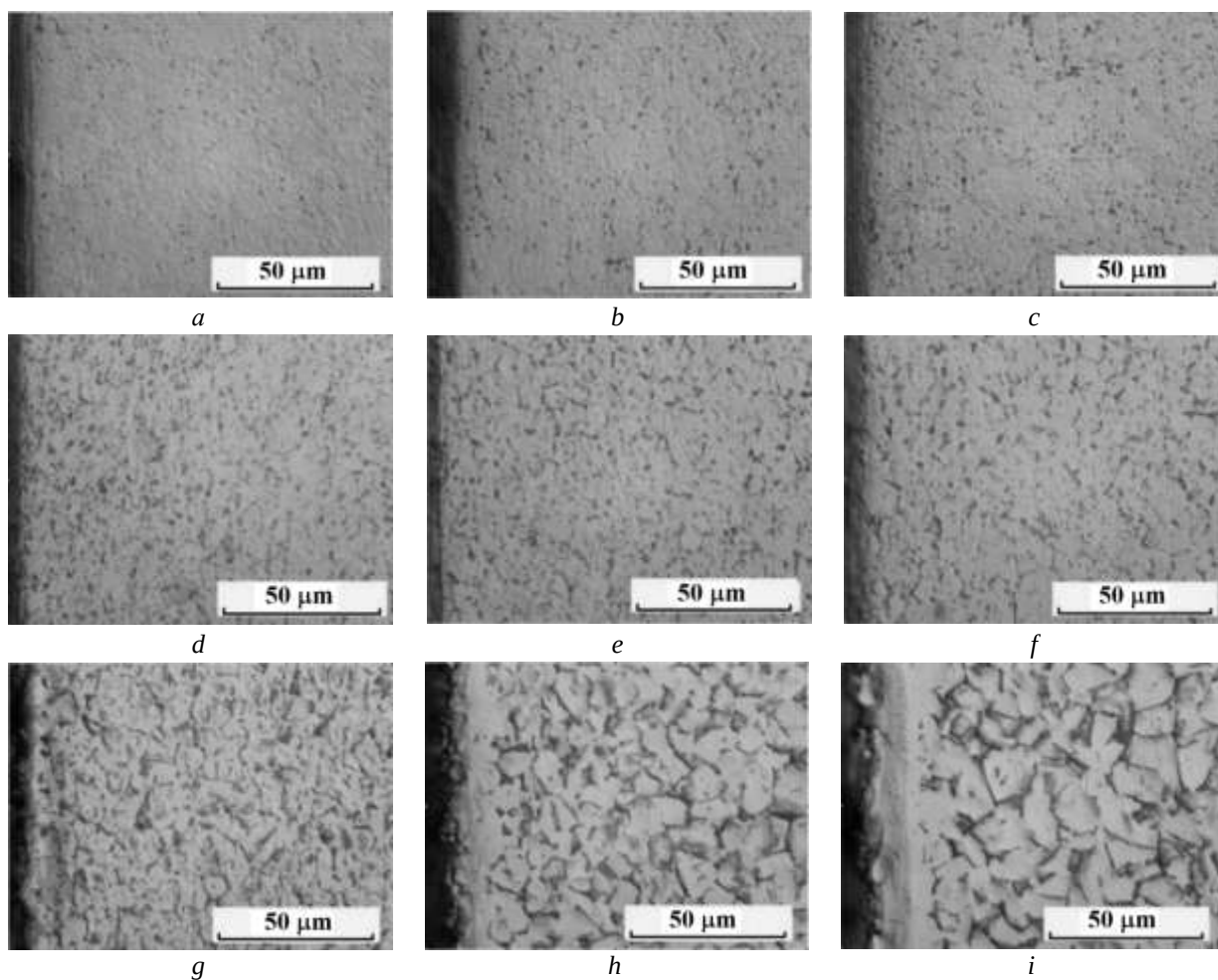


Fig. 2. Microstructure of the Zr-1Nb surface layer after diffusion saturation with nitrogen at 550 °C (a, b, c); 650 °C (d, e, f); 750 °C (g, h, i) during 1 h (a, d, g); 5 h (b, e, h); 10 h (c, f, i)

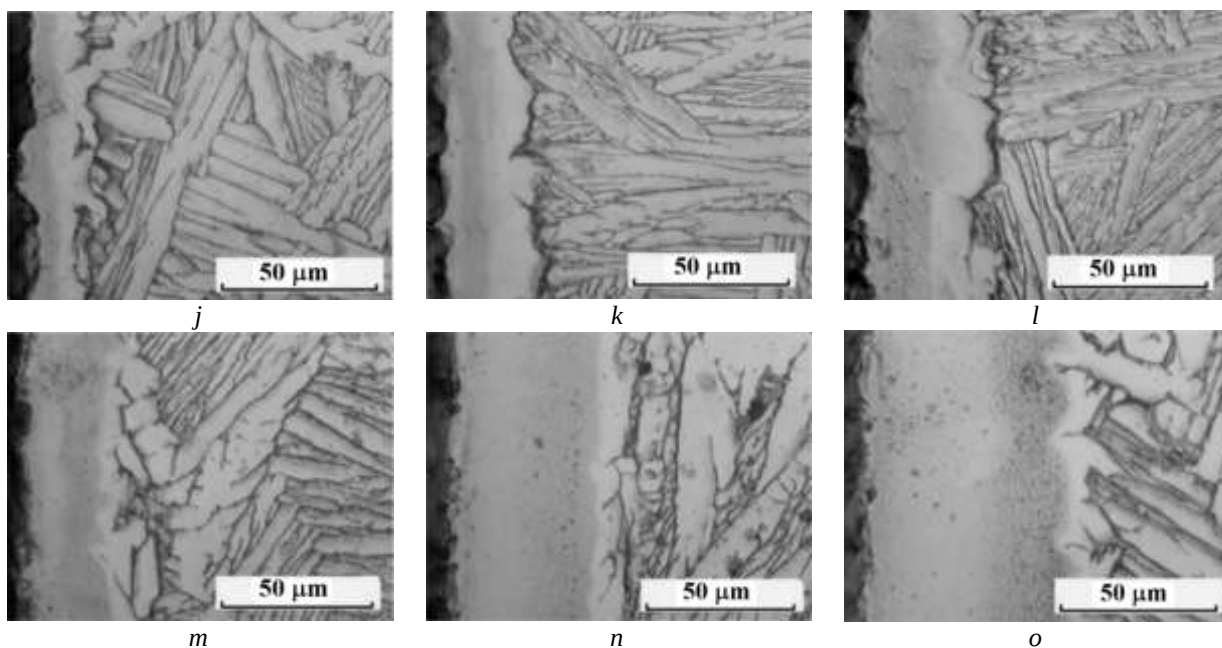


Fig. 2. Microstructure of the Zr-1Nb surface layer after diffusion saturation with nitrogen at 850 °C (j, k, l); 950 °C (m, n, o) during 1 h (j, m); 5 h (k, n); 10 h (l, o)

Thus, with increasing time-temperature regimes of nitrogen saturation, the intensity of α -Zr reflexes decreases and while the intensity of ZrN and Zr₂N reflexes increases on the other hand. This is due to the increase in the depth of the compound (ZrN and Zr₂N) layer, which increases its shielding effect for the α -Zr sub-layer. According to the results of XRD analysis, the ZrN and Zr₂N reflexes on the surface of the Zr-1Nb alloy after nitriding are fixed starting from the treatment at 650 °C for 5 h. Therefore, it can be assumed that at a lower nitriding temperature, zirconium nitrides (ZrN, Zr₂N) of significant thickness are not formed.

CONCLUSIONS

1. It was found that with increasing time-temperature regimes of diffusion saturation with nitrogen, the intensity of the zirconium nitride reflexes increased. This was explained by the increase in the depth of the compound (ZrN and Zr₂N) layer.

2. It was shown that ZrN and Zr₂N reflexes on the surface of the Zr-1Nb alloy were observed after nitriding from at 650 °C for 5 h, which is consistent with the affinity of zirconium for nitrogen.

3. It was established that with an increase in temperature from 550 to 950 °C and exposure time from 1 to 10 hours of nitriding, the modified layer depth increased from 2...660 and 0.061...0.745 μm, respectively.

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ВПЛИВ ДИФУЗІЙНОГО НАСИЧЕННЯ АЗОТОМ НА СТРУКТУРУ ТА МІКРОТВЕРДІСТЬ ПОВЕРХНЕВОГО ШАРУ СПЛАВУ Zr-1Nb

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Наведено дані щодо впливу дифузійного азотування на структуру, фазовий вміст та мікротвердість поверхневого шару сплаву Zr-1Nb. Показано, що з підвищенням температури та тривалості дифузійного насичення азотом інтенсивність рефлексів α -Zr зменшується, а інтенсивності рефлексів ZrN та Zr₂N зростають. Таке явище пояснено збільшенням товщини шару нітридів ZrN і Zr₂N, через що зростає його екранувальний ефект для підшару α -Zr. Показано, що рефлекси ZrN та Zr₂N на поверхні сплаву Zr-1Nb після азотування фіксуються починаючи з оброблення при 650 °C упродовж 5 год. Показано вплив температурно-часових параметрів насичення на зміну товщини азотного шару та мікротвердість поверхні. Зроблено висновок, що застосування дифузійного насичення азотом є перспективним методом впливу на мікротвердість та структуру сплаву Zr-1Nb.