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## MICROSTRUCTURE OF THE DIFFUSION LAYER OBTAINED IN Ti6Al2Cr2Mo ALLOY DURING GLOW DISCHARGE NITRIDING

### ABSTRACT

This paper presents the results of metallographic, X-ray, and TEM examinations of the microstructure and the sub-structure of the diffusion layer that underlies the TiN + Ti<sub>2</sub>N layer produced by glow discharge nitriding of the Ti6Al2Cr2Mo alloy. The metallographic examinations show that a two-phase zone  $\alpha + \beta$  - its thickness increasing with the increasing process temperature - can be observed underneath the nitride layer after half an hour of nitriding at 940°C, when the core of the sample has an  $\alpha$ -phase structure. The presence of the glow discharge assisting the nitriding process accelerated the thickening of both the nitride zone and the diffusion layer. Morphology of  $\alpha$ -phase grains changed as well. The grain length-to-thickness ratio decreased. X-ray examinations revealed the presence in the substrate structure of two kinds of solid solution with the  $\alpha$  titanium matrix. TEM analysis showed a state of certain ordering of the crystalline lattice and, locally, a tweed-type structure of the  $\beta$  phase.

**Keywords:** two-phase titanium alloy; glow discharge; nitriding; TEM microstructure; phase composition.

### 1. INTRODUCTION

The increasing use of titanium alloys in industry is still restricted by their poor frictional wear resistance. Therefore, there is a need for a new technology, which would increase this resistance and modify advantageously the structure of the substrate, so as to improve the fatigue strength of the alloys. Glow-discharge nitriding is a promising process here: it increases significantly the surface hardness, and thereby the frictional wear resistance, and also slightly improves the corrosion resistance [1-3].

A very important cognitive aspect in nitriding of the titanium alloys is the formation of a diffusion layer with a specified structure which influences mechanical properties of the two-phase titanium alloy by modifying the particle size and the amount of phases formed as a result of the  $\beta$  phase decomposition. The most advantageous volumetric content of the  $\alpha$  phase in this zone appears to be about 80%, with a certain optimum length and thickness of the grains and an appropriate spacing between them [1]. There are several techniques which can produce such a structure in a given alloy, and do it successfully even when its individual batches differ slightly in their chemical composition and initial structure. The success depends on the knowledge of the mechanism of the initial stage of the metastable  $\beta$  phase decomposition and on the way in which this stage is utilised to achieve a sufficiently strong hardening effect. It is however not known how to control the decomposition of the  $\beta$  phase during nitriding and, thus, how to modify the structure effects of the diffusion layer so as to improve the mechanical properties of titanium alloys [2-5]. It is an essential advantage of the  $\beta \leftrightarrow \alpha$  phase transformation that it generates low structural stresses, which is due to small differences between certain dimensions of the elementary cells of the parent phase and of the phases that are formed from it [5-6]. Greater stresses can appear when the decomposition reaches a certain stage, when the morphology of the

structural components undergoes changes, or when lattice deformation occurs as a result of a volumetric difference between the matrix and the precipitates - an effect known as phase work hardening [7-10]. The opinion about the mechanism of the initial stage of the decomposition of the  $\beta$  phase has not been settled yet [6-8]. The relevant literature reports suggest that this stage can proceed in various ways and that the intermediate decomposition phases can undergo further changes until an equilibrium structure forms. It is suggested that this process may have features of a spinodal decomposition which results in the formation of two solid solutions, partially or totally ordered. The more stable solid solution evolves towards a B2 type superstructure and can reach the ordering of the  $DO_3$  or  $A_7B$  type. Like any other metastable phase with the bcc lattice, a  $\beta$  phase that is less saturated with stabilisers may have a rhombic or rhombohedral lattice distortion, always associated with a change of the elastic constants  $1/2(c_{11} - c_{12})$  and  $c_{44}$ , which increases the instability of the crystal lattice. When the saturation of the  $\beta$  phase with stabilisers is low, it may decompose into the  $\beta + \alpha'$  phases, whereas at a greater saturation the decomposition into the  $\beta + \omega$  phases occurs. The decomposition mechanism is based on the diffraction effects which represent the positions and displacements of atom characteristics of  $\omega$  and  $\alpha$  ( $\alpha'$ ) phases [14,15].

The aim of the present study was to analyse the micro- and sub-structure in the Ti6Al2Cr2Mo (numbers are wt. %) diffusion layer subjected to glow-discharge nitriding within an appropriately selected temperature range and under the process conditions that eliminate the possibility of recrystallisation of the core structure.

## 2. MATERIAL AND METHODS

The chemical composition of the examined Ti6Al2Cr2Mo alloy is presented in Table 1, while the parameters of the glow-discharge nitriding process followed by cooling of the samples in vacuum to room temperature are shown in Table 2. The phase composition and the properties of nitride layers are described in refs. [3,4].

The microstructure was examined by means of a Neophot 2 optical microscope. Longitudinal cross-sections were prepared by polishing and etching in 96% $H_2O$ , 2% $HF$ , 2% $HNO_3$  solution. The phase composition of the diffusion layer was analysed by means of a Philips PW1720 X-ray diffractometer, with  $CuK_{\alpha}$  radiation applied. Transmission electron microscopy analysis (TEM) was performed with a Philips CM20 electron microscope equipped with selected area diffraction (SAD).

**Table 1.** Chemical composition of the examined Ti6Al2Cr2Mo alloy

Element	Al	Cr	Mo	Fe	Si	Ti
	6.3	2.1	2.0	0.4	0.1	balance

**Table 2.** Parameters of the glow discharge nitriding processes

Process	Nitriding temperature [°C]	Nitriding time [h]	Thickness of the compound layer [μm]	Thickness of the diffusion layer [μm]
1.	940+880+815, vacuum cooling	1.0 +1.0+1.0	20	60
2.	940+815, vacuum cooling	4.0+1.0	20	60

### 3. RESULTS

The temperature of glow-discharge nitriding process - 940°C - and other process parameters corresponded to the stability range of the  $\beta$  phase in the parent material. They favoured transformation into a two-phase structure through shearing, as can be inferred from the analysis of the core microstructure (Fig.1 b and d). The diffusion layer contains  $\alpha$  phase grains, with varying ratio of length-to-thickness, and a dispersive, lamellar mixture of  $\alpha$  and  $\beta$  phases formed as a result of the metastable  $\beta$  phase decomposition, again through the shear mechanism (Fig.1, a and c). The microstructure of the diffusion layer with a dominant content of the  $\alpha$  phase is characteristic of titanium alloys subjected to isothermal annealing within the two-phases temperature range. It means that nitrogen diffusing into the alloy causes a stabilisation of the  $\alpha$  phase and thereby shifts the  $\beta \rightarrow \alpha + \beta$  transformation temperature towards higher range values.

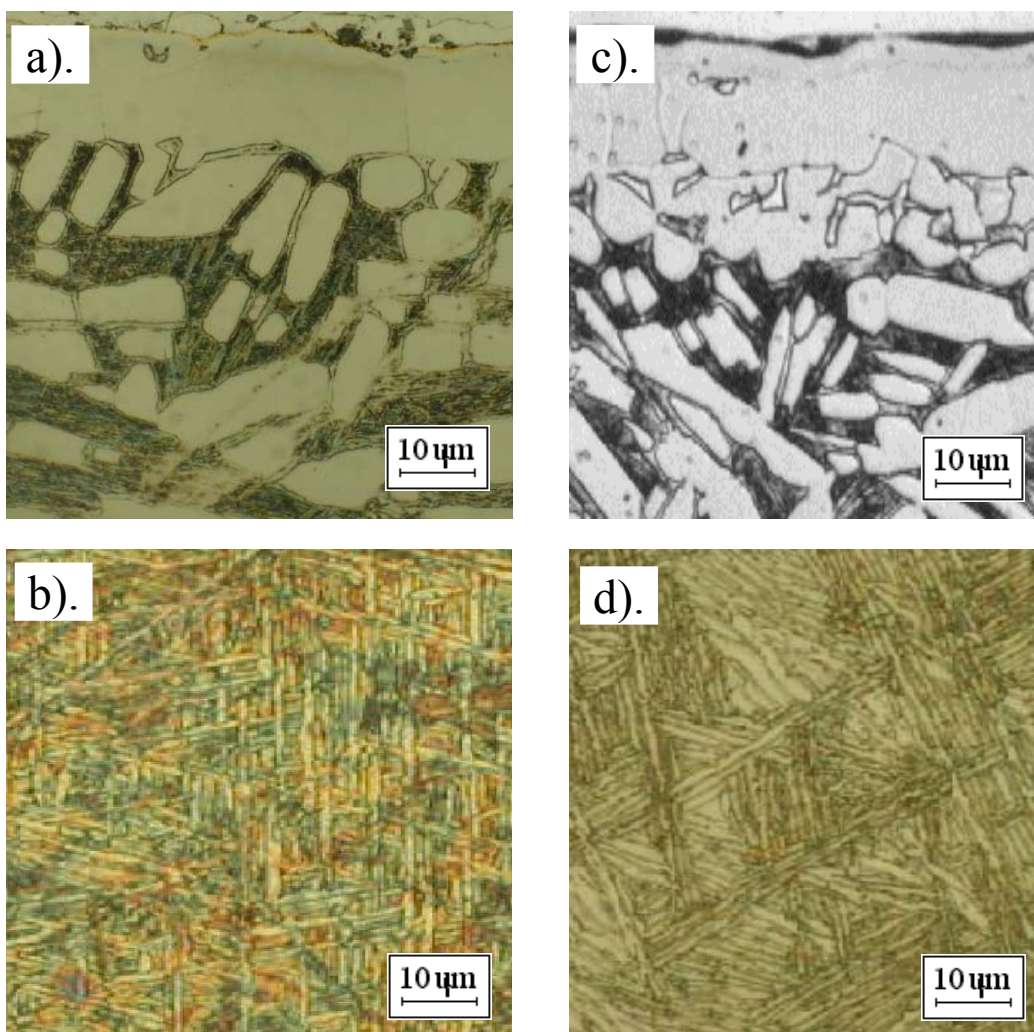


Fig.1. Microstructures of the nitrided layer and the diffusion layer (a,c) and of the core (b,d) of the Ti6Al2Cr2Mo titanium alloy, formed during the process 1 (a,b) and the process 2 (c,d), (Table1)

The change of glow-discharge nitriding parameters from those employed in process 1 into those of process 2, did not affect substantially the thickness of the TiN+Ti<sub>2</sub>N nitride layers or the morphology of the two-phase structure of the diffusion layer and the core. The only observed differences included: coagulation of the  $\alpha$  phase within the 15- $\mu$ m thick layer, formed directly beneath the nitride layer after the process 2 (Fig.1c), and an increased share of the  $\alpha$  phase in the diffusion layer after the process 1 [2,3]. In both cases, a well-marked boundary was observed between the diffusion layer and the structure of the core, formed as a result of the transformation of the non-nitrided  $\beta$  phase.

The growth of  $\alpha$ -phase grains started from grain boundaries in the  $\beta$  phase (Fig.1 b and d). Its rate was higher along the habit planes than in the direction perpendicular to them, which is consistent with the Zener-Hillert theory [8]. The  $\alpha$ -phase grains were not observed to grow from the inter-phase boundaries towards the interior of the  $\beta$  grains of the matrix, which typically occurs when titanium alloys are annealed at high temperatures. Figs. 1a and c show evident differences between morphologies of individual  $\alpha$  grains present in the diffusion zone.

### 3.1. X-ray phase analysis (XRD)

The phases presented in the substrate were identified on the basis of interferences (peaks) in crystallographic planes of the  $\alpha$  phase (Table 3): 10.0, 00.2, 11.0, 20.0 and 00.4, and of the  $\beta$  phase (Table 4): 110, 200 and 211. As the peaks were close to each other, due to the presence of certain plane families of phases  $\alpha$  and  $\beta$  (e.g., 00.2 $\alpha$  and 110 $\beta$ ), only those peaks that belong undoubtedly to a given lattice type were taken into account in calculations. The peaks were doublets or showed asymmetry, which indicated that the examined structures were modifications of solid nitrogen solutions in  $\alpha$ -Ti and  $\beta$ -Ti phases.

**Table 3.** Characteristic of the interferences (peaks) used for identifying the  $\alpha$  phase in the diffusion layer

Process	(hkl)	2 $\theta$	D <sub>hkl</sub>
1.	10.0 blurred	35.1811	2.441411
	00.2 blurred	38.4194	2.346469
	11.0 blurred	63.1265	1.472759
	20.0 (doublet)	86.7201 (86.8902)	1.122810 (1.12105)
	11.2 $\omega$	40.1443	
2.	10.0 blurred	35.1689	2.551710
	00.2 blurred	38.3895	2.344728
	11.0 blurred	64.1031	1.452659
	20.0 (doublet)	86.7713 (86.8565)	1.122280 (1.12140)
	11.2 $\omega$	40.1247	

**Table 4.** Characteristics of the interferences (peaks) used for identifying the  $\beta$  phase in the diffusion layer

Process	hkl	2 $\theta$	d <sub>hkl</sub>
1.	110 blurred	38.2337	2.3682
	200 (doublet)	54.4278 (54.6035)	1.68571 (1.68015)
	211 (doublet)	69.9352 (70.0505)	1.393134 (1.34318)
2.	110 blurred	37.8940	2.374240
	200 (doublet)	53.0729 (53.4473)	1.725508 (1.714301)
	211 (doublet)	70.0708 (70.2110)	1.342839 (1.34050)

Apart from the above-mentioned peaks, interferences at  $2\theta$  angles of 40.144 (process 1) and 40.124 (process 2) were observed. They corresponded to the 11.2 reflection of the  $\omega$  phase. The other peaks of this phase coincided with the reflections of the  $\beta$  phase. This was one of the reasons for the interferences from the  $\beta$  phase for the alloy subjected to the process 1 to be broader. The fact that the values of the  $2\theta$  angles measured after the process 2 were greater, compared to those after the process 1, could mean that the lattice constant of the  $\beta$  phase formed in the process 1 is smaller than that of the  $\beta$  phase formed in the process 2. In turn, the smaller value of the lattice parameter suggested a greater content of alloying elements. The additional interference in close vicinity to the  $110\beta$  peak on the side of small angles can be interpreted as 10.0 peak of the  $\alpha$  phase enriched with alloying elements (Tables 2 and 3). The fact that the interferences from the  $\alpha$  and  $\beta$  phases are more blurred in the alloy subjected to the process 1 can be explained by microsegregation of alloying elements, dispersion of particles, and the presence of microstresses. In conclusion, the structure in the diffusion layer - under the conditions of the process 2 - comes closer to equilibrium and the hardening effect is probably weaker. The residual stress within the sample surface with diffusion layer was measured with diffraction line shifting ( $\sin^2\Psi$  method). The obtained results produced values around  $-1500$  MPa.

### 3.2. Transmission electron microscopy (TEM)

#### 3.2.1. Process 1.

Microphotographs of the  $\alpha$  phase (Fig.2a) show a characteristic shear bands contrast, representing pre-precipitation of phases in the form of flat agglomerates [5]. The effects of diffusion dispersion and streaks could be seen in diffraction patterns (Fig.2b), which confirms that the initial stage of decomposition proceeded by certain concentration fluctuation waves. This suggests that the pre-precipitates of the secondary phases were present or that the crystalline structure was ordered.

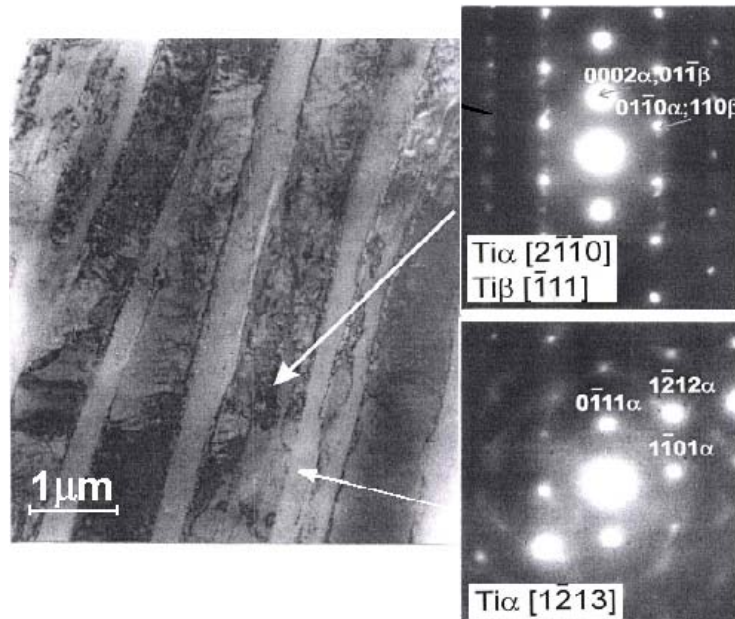


Fig. 2. TEM microstructure (a) of the diffusion layer after the process 1, and the indexed electron diffraction patterns (b,c)

A relatively low concentration of the elements that stabilise the  $\beta$  phase in the alloy and, additionally, its destabilisation by nitrogen atoms, seem to indicate that both phenomena mentioned above took place. Local differences in the concentration of alloying elements bring about differences in the values of the structural factor and induce elastic stress fields in the matrix. Cooling from the two-phase temperature range could result in the  $\beta \rightarrow \omega$  transformation, whereas cooling from above the varying solubility line should lead to the  $\beta \rightarrow \alpha$  transformation, due to a uniform saturation with the  $\beta$  stabilisers. The process was observed, when the examined alloy [12] was cooled directly from the temperature of 940°C, where the interference profiles were not blurred. In this study, the XRD results did not confirm the occurrence of the  $\beta \rightarrow \omega$  transformation.

### 3.2.2. Process 2.

Due to a relatively longer nitriding time in this process, decomposition and ordering of crystalline structure are more complete. The images of reciprocal lattice (Fig.3b) did not show streaks and diffusion dispersion effects, despite the presence of the  $\omega$  phase.

The results of the present study suggest that the conditions under which the glow-discharge nitriding was carried out – namely, temperatures close to the temperature of the polymorphic transformation  $\beta \rightleftharpoons \alpha + \beta$  and cooling process conducted in vacuum – lead to microsegregation of alloying elements as well as to the stabilisation of the  $\beta$  phase and to the enrichment of this phase with  $\beta$ -generating elements, probably at the expense of Al depletion.

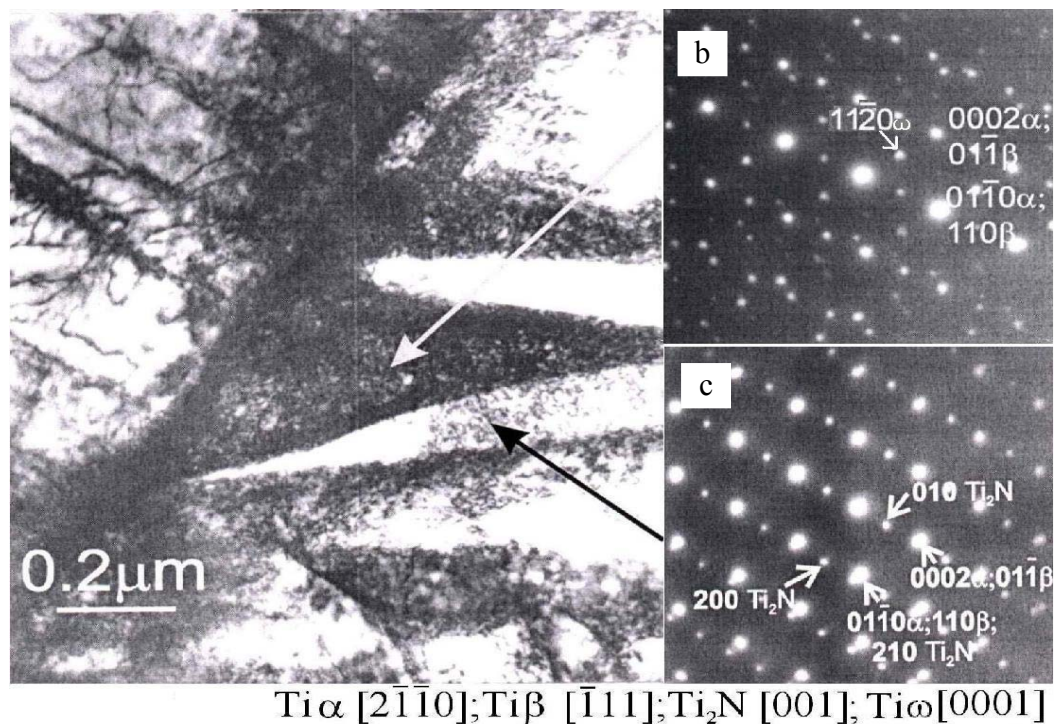


Fig. 3. TEM microstructure (a) of the diffusion layer after the process 2 and the indexed electron diffraction patterns (b,c)

#### 4. CONCLUSIONS

The conditions under which the glow-discharge nitriding process was carried out in the present experiments favour the decomposition of the metastable  $\beta$ Ti solid solution into two  $\beta$  phases that differ from one another by their chemical composition. The  $\beta$  phase which is richer in alloying elements and which is probably much less abundant, undergoes a transformation into the  $\omega$  phase, whereas the  $\omega$  phase containing less alloying elements is transformed into the  $\alpha$  phase. Moreover, the  $\alpha$  phase is also formed from the  $\omega$  phase. The diffusion of nitrogen stabilises the  $\alpha$  phase and changes the solubility range of  $\alpha+\beta\leftrightarrow\beta$ , shifting this range towards higher temperatures.

In the glow-discharge nitriding under the conditions of the process 2, precipitation is enhanced, including the precipitation of the  $Ti_2N$  phase, and the magnitudes of structural stresses are reduced (Fig.2c).

The conditions of process 2 do not enhance grain growth in the diffusion layer and in the core, nor do they affect the thickness of titanium nitride layer.

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