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MODIFYING THE STRUCTURE AND SURFACE PROPERTIES OF Ti6Al4V ALLOY BY CARBONITRIDING IN FLUIDIZED BED

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ABSTRACT

The Ti6Al4V alloy is known as being one of the most widely used biocompatible alloys and not only that. The study is based on experienced research of the hardening in a fluidized bed and applied to samples of Ti6A14 in laboratory conditions. The carbonitriding has been accomplished on an exterior electric heating reactor. It has been examined the influence of the heat and the duration of the thermochemical treatment out of economy interests, the flow has been made with a mix of CH_4 and NH_3 (5% concentration). The results have been examined through hardness (HV5), metallographic microstructures and micro hardness in section (micro HV).

KEYWORDS: titan alloy, Ti6Al4V, carbonitriding, FBT, Fluidized bed

1. Introduction

Carbonitriding represents a thermochemical treatment, with a wide application on steels because of the advantages it has concerning the modifications of chemical structure and superficial properties, after the application of a hardening and return treatment. A primary treatment applied to the surface is recommended on steels to put the value of the resources after the carbonitriding.

The influence of different types of superficial (1) has been studied, such would be the lustre, the sanding, the processing with steel shots of samples of Ti6Al4V before the carbonitriding made in plasma.

The insertion of argon gas and spraying with carbon atoms from a graphite damper in the plasma workspace [N_2-Ar-C (g)] can lead to the production of the desired nitrate, phases of carbide and nitrocarbide on the surface and inside titanium alloy samples and can lead to changes in the microstructure. That is why the samples have been carbonitrided in N_2/Ar (70% N_2 + 30% Ar) plasma at a 650 ºC temperature, for 5 hours. The carbon atoms have been generated in the graphite hollow cathode, where carbon atoms spraying takes place, during the nitriding process. The results lay out the facts that there exists a forming of a thicker layer of TiN and

The hardness after carbonitrating in fluid layer depends on the duration of the treatment and the working temperature. Carbonitrures in the sample are blown with sand but with irregular topography. The samples processed with steel shots and the polished ones have smoother surfaces, while the nitride and carbonitride layer is smaller. The hardness of the Ti6Al4V carbonitrided alloy on a 650 °C temperature could get to values close to 850 HV on the surface and gradually decreases till the substrate value (300 HV).

Another example is nitriding and nitrocarburizing of gun pipes (2). A gun pipe made of titan alloy (Ti6Al4V) has been nitrocarburized in a fluidized bed at a rough 788 °C temperature for 6 hours. The composition of the reacting gas was: ammonia (NH_4) 50%, natural gas (CH_4) 5% and nitrogen 45%. The result has been the obtaining of a pipe with a nitrocarburized surface. Its characteristics were the following:

- increase in the projectile speed;
- the pipe had a smooth finish;
- the pipe had a reduced friction;
- the pipe had a bigger wear resistance;
- the hardness of the pipe was significantly increased;
- the distortion resistance of the pipe was a good one even after repeated shots;
- the corrosion resistance was improved.

Notations and abbreviations

FB – Fluidized Bed
FBT – Fluidized Bed Technology
CN – CarboNitriding
FBCN – Fluidized Bed CarboNitriding

One of the advantages of using the fluidized oven and funnels at the edges of the titanium pipe is that the processing time for completion of the same results in a fluidized oven is reduced from 24 hour to 6 hours, and the temperature is reduced from 980-1010 °C to 760-870 °C. This decrease of temperature is considerable for the treatment of a titan alloy pipe or any titan alloy because it is a lot under the melting point. And so, the distortion risk has been importantly reduced or even deleted.

The Ti6Al4V alloy treatment by ionic carbonitriding was studied regarding the moulder of nitrides and carbides layer through. To this purpose, there has been used a plasma room of nitriding and a hollow graphite cathode using nitrogen and argon. The titanium samples and Ti6Al4V have been carbonitrided in plasma N_2-C (g), at temperatures between 500 °C and 1000 °C. The generation of gas carbon in the plasma atmosphere is possible through ionic bombardment of a graphite target strategically emplaced in the interior of the room. The results indicate the fact that the N_2-C atmosphere is suitable to such a treatment type, creating layers of TiN, T_2N and $TiC_{0,3}N_{0,7}$, compounds with the thickness of about 2.0 µm when the treatment is made at low temperatures (550-600 °C) and 35.0 µm for treatments at higher temperatures (1000 °C).

The achievement of carbonitriding of Ti in fluid state respects Fig. 1 such as using initial precursors, marsh gas and ammonia stable in normal conditions. At the conditions of the thermochemical, the instable thermodynamic precursors decompose (Fig 1).

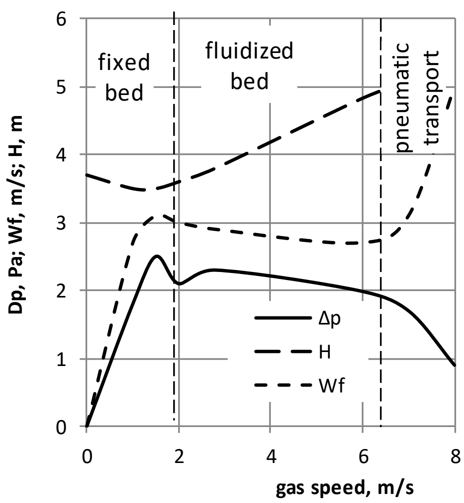

Fig. 1. *The fluidized bed is limited by the fixed bed and the pneumatic transport*

The employment of the flow layer at thermochemical treatments applied in superficial modifications is made with the following remarks:

- the environment of the flow layer is thermally active and chemic in some gas dynamic functioning conditions
- the environment of the flow layer is characterized by a high consumption of technological gases, because the resulted gases and the initial coloured traces also provide the flow phenomenon.
- the impact of the carbonitriting in flow layer technology over the environment is practically reduced at a small quantity of CO_2+steam of water that results after the final combustion of the fuel substances at the reactor exit.

2. Experimental conditions

The objective of the experiments in laboratory condition has been made to emphasize the possibility of superficial modifications concerning the Ti6Al4V alloy. Furthermore, it tracks the capacity of the medium to create a thermal activity and a chemical one by controlling some technological factors.

Experimental model is realized so that physics and specific chemical phenomena can be highlighted: fluidity, the thermal and chemical decomposition of the chemical reactions (Fig. 1, Fig. 2).

There have been used samples of Ti6Al4V alloy taken from a material used to making dentures. The material is made by the Zeno corporation (Germany) having the chemical composition and the properties guaranteed in the following table:

chemical composition of the Ti6Al4V alloy is being presented in the (Table 2).

Table 1. *TI6Al4V alloy characterization*

Type Titanium Alloy grade 5	u.m.	
Density	g/cm3	4.3;
Vickers Durity	HV 5/30	350;
CTE (25 - 500 °C)	10-6 K-1	10.3;
Constituents	%	Al : 5.5 - 6.75
		V : 3.5 - 4.5
		More : <0.4
		Rest : Ti
Limit Break	Mpa	930
Tehn Limit of Elasticity 0,02	MPa	900
Elongation		10
Melting point	°C	1604 - 1660
	F	2919 - 3020

The samples have been cut and finished on vertical surfaces with sandpaper 300. The vertical surfaces are the ones that are important for the thermochemical treatment in fluid layer. The samples have been tied with wire to a loading device. It is known the position influence of the surfaces of the oven, which is important at thermal treatments and thermochemical treatments in fluid layer and not only. The following step consists of emplacing the samples of Ti6Al4V alloy in the middle of the fluid layer. In the carbonitriding in fluidized beds process it is necessary that the following factors be taken into consideration:

- samples positioning in the oven
- carbonitriding temperature.
- the duration of the process.
- the chemical activity of the environment (concentration of ammonia or flow of ammonia).

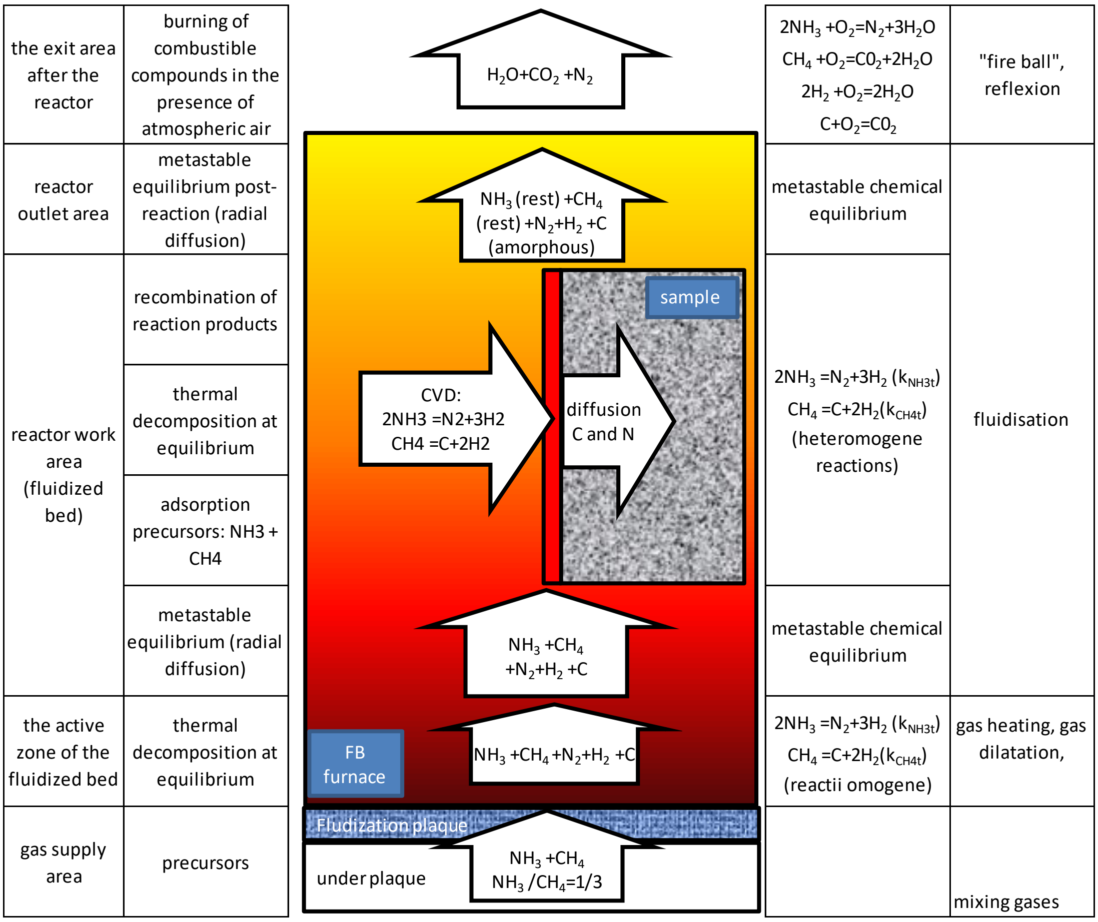

Fig. 2. *Physical and chemical processes on fluidized bed nitrocarburizing*

For the development of the experiments it has been used a classical factorial matrix, taking into consideration the following factors and the following levels: temperature: 930 °C; 850 °C; 750 °C and treatment duration: 60 min; 90 min; 120 min (Table 2). The relatively small durations of treatment are due to the chemical and thermal activities of the environment which are higher than when done in gas and smaller than the ones in salts baths, and the fact that the loading and unloading are done much faster due to working with an open enclosure.

Table 2. *Experimental regimes for FBNC applied to Ti6Al4V alloy samples*

exp. no.	temperature	time	gas composition
u.m.	°C	min	%
1	750	60	95% methane + 5% amoniac
2		90	
3		120	
4	850	60	
5		90	
6		120	
7	930	60	
8		90	
9		120	

3. Results and dissection

The structural changes have been analysed through metallographic analyses. The samples are sectioned at about ½ from their original height (original height of the disc). Investigation methods follow:

- pointing the chemical modifications on the surface and the chemical composition profile from the surface to the core;
- pointing the structure modifications on the surface and the transition zone towards the core;
- pointing the properties modifications on the surface and the transition zone to the core.

The investigations have been conducted in laboratory on significant samples, in standard stated conditions and have been conducted through:

- microstructure in transversal section for highlighting the structural modifications which determine the superficial properties modifications;
- Vickers hardness on surface, for highlighting superficial properties modifications.

The Ti6Al4V alloy samples have been sectioned at half their height and have been emplaced in two-component resin. After hardening, the grinding was achieved manually using sandpapers. The polish took place on moist felt with the polish agent 3-A-S.

The metallographic attack has the role of highlighting the structure elements in the new section. That reacts with the surface of the sample differentiated depending on the microrelief and the local free energy. The image obtained with the help of the metallographic microscope in different sizes highlights structural constituents, flows and superficial thermo-chemical treated zone.

The most used chemical reactive for the metallographic attack of titan and titan alloys is the Kroll reactive which has the following chemical composition: 100 ml distilled water, 1-3 ml hydrofluoric acid, 2-6 ml nitric acid.

The reagent concentration may vary in wide scales depending on the alloy type. The reagent gives a dark brown coloration for the β phase.

Titan can be attacked and coloured using the Weck reagent, which has the following chemical composition: 100 ml distilled, 5 g ammonium biflorure.

The microstructure in the transversal section was made on the un-attacked surface for highlighting inclusions and on the attacked surface

In Fig. 5 to 13 are presented the representative microstructures for the nine probes carbonitrated in fluidized bed.

Fig. 4. *Sample Ti6Al4V attacked with cu Kroll reagent*

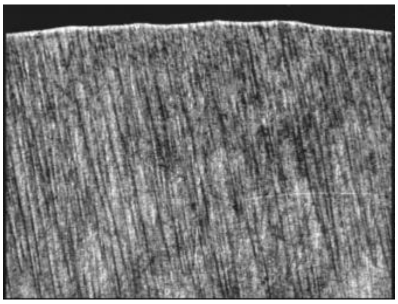

Fig. 5. *Microstructure of the first sample of Ti6Al4V alloy corbonitrided at 750 °C/60 min (zoom: 100x)*

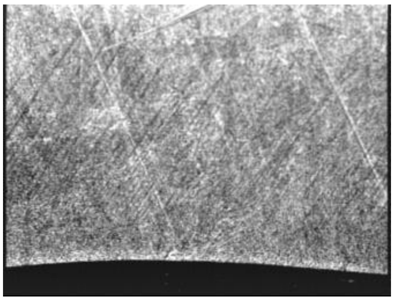

Fig. 6. *Microstructure of the second sample of Ti6Al4V alloy corbonitrided at 750 °C/90 min (zoom: 100x)*

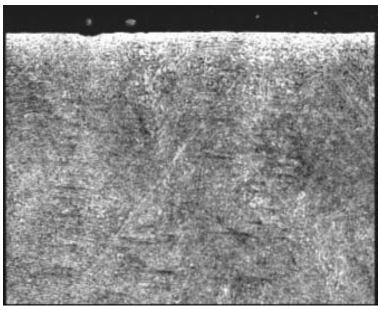

Fig. 7. *Microstructure of the third sample of Ti6Al4V alloy corbonitrided at 750 °C/120 min (zoom: 100x)*

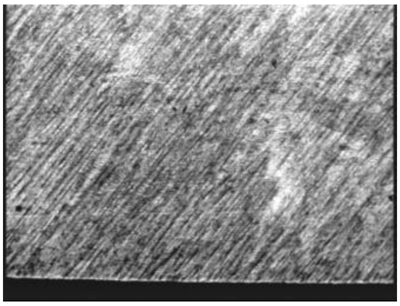

Fig. 8. *Microstructure of the fourth sample of Ti6Al4V alloy corbonitrided at 850 °C/60 min (zoom: 100x)*

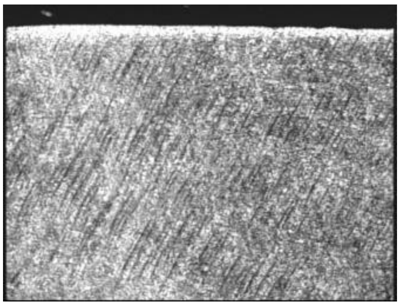

Fig. 9. *Microstructure of the fifth sample of Ti6Al4V alloy corbonitrided at 850 °C/90 min (zoom: 100x)*

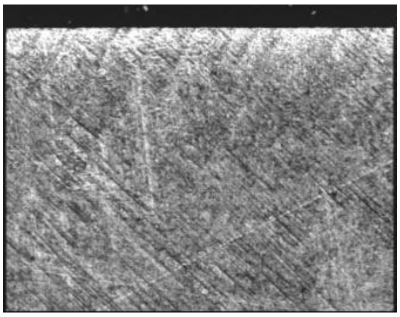

Fig. 10. *Microstructure of the sixth sample of Ti6Al4V alloy corbonitrided at 850 °C/120 min (zoom: 100x)*

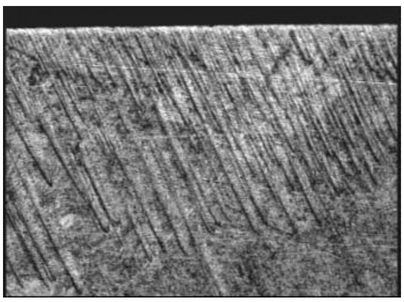

Fig. 11. *Microstructure of the seventh sample of Ti6Al4V alloy corbonitrided at 930 °C/60 min (zoom: 100x)*

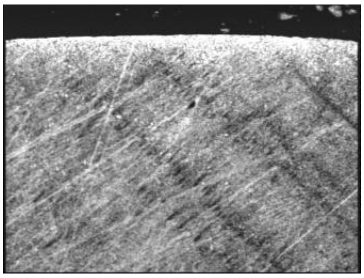

Fig. 12. *Microstructure of the eight sample of Ti6Al4V alloy corbonitrided at 930 °C/90 min (zoom: 100x)*

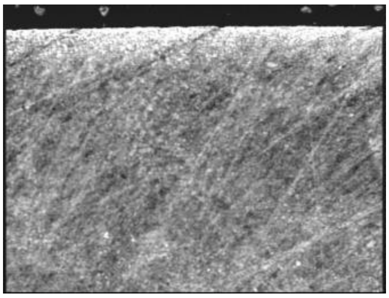

Fig. 13. *Microstructure of the ninth sample of Ti6Al4V alloy corbonitrided at 930 °C/120 min (zoom: 100x)*

Table 3. *Medium layer depth for Ti6Al4V carbonitrided in fluidized bed (FBCB)*

sample	time	temperature	depth layer
m.u.	min.	°C	mm.
1	60		0,01
2	90	930	0,02
3	120		0,03
4	60		0,01
5	90	850	0,03
6	120		0,03
7	60		0,01
8	90	750	0,02
9	120		0,02

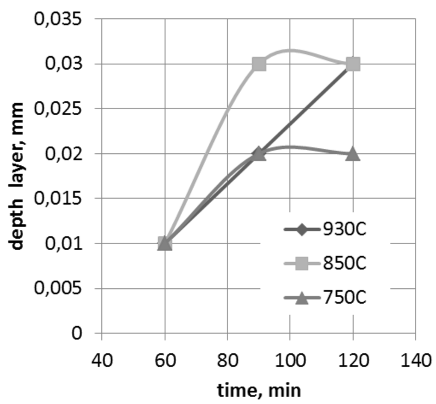

Fig. 14. *Ti6Al4V Layer depth after FBCN*

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Table 4. *HV5 Vickers hardness after CNFB*

Sample Nr	d^2	HV_5	HV Final	Temperature	Time
u.m.	mm	daN/m^2	daN/m^2	°C	min.
1	0.142	459.83	437.48	930	60
	0.149	417.64			
	0.146	434.98			
2	0.146	434.98	435.02	930	90
	0.147	429.08			
	0.145	441.00			
3	0.145	441.00	515.03	930	120
	0.151	406.65			
	0.115	697.45			
4	0.139	479.89	466.70	850	60
	0.144	447.15			
	0.140	473.06			
5	0.129	557.18	535.41	850	90
	0.135	508.75			
	0.131	540.29			
6	0.121	633.29	695.64	850	120
	0.111	752.54			
	0.115	701.10			
7	0.147	429.08	425.58	750	60
	0.145	441.00			
	0.151	406.65			
8	0.130	548.64	566.19	750	90
	0.128	565.92			
	0.126	584.03			
9	0.142	459.83	439.49	750	120
	0.149	417.64			
	0.145	441.00			

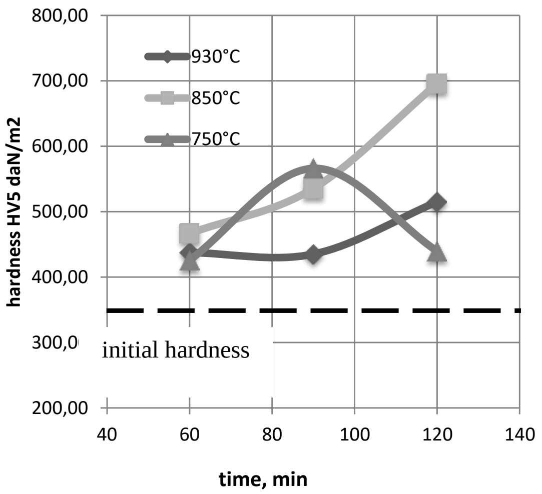

Fig. 15. *Hardness after BFNC*

The Ti6Al4V alloy hardness after carbonitrating in fluidized bed are shown in table below and interpreted in Fig. 13.

The hardness after carbonitrating in fluid layer depends on the duration of the treatment and the working temperature.

3. Conclusions

- A carbonitrating layer develops on all Ti6Al4V alloys after all experiments of carbonitrating in fluid layer;
- the hardness of the Ti6Al4V alloy after carbonitriding in fluidized bed increases on all experimented samples;
- the hardness after FBCN increases with the carbonitriding temperature;
- for every treatment temperature the hardness has a maintenance duration of maximum 2 hours;
- there has been observed a maximum in increasing the layers thickness and its hardness at 850 °C, for a 2-hour duration (Fig. 9).

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