

HYBRID CARBON LAYERS FOR MEDICAL APPLICATION

DOROTA NOWAK^{1*}, PIOTR NIEDZIELSKI²

¹ TECHNICAL UNIVERSITY OF LODZ,
INSTITUTE OF MATERIALS SCIENCE AND ENGINEERING
1/15 STEFANOWSKIEGO ST., 90-924 LODZ, POLAND

² TECHNICAL UNIVERSITY OF LODZ,
INSTITUTE OF MATERIALS SCIENCE AND ENGINEERING
1/15 STEFANOWSKIEGO ST., 90-924 LODZ, POLAND

* E-MAIL: DKARGULEWICZ@O2.PL

Abstract

Carbon layers thanks to their advantages (high biocompatibility, good wear resistance, high corrosion resistance) found the application in medicine. The authors of presented work have obtained improvement of above-mentioned properties (high hardness) with use of hybrid RF PACVD method. Carburizing of the AISI 316L stainless steel is connected with risk of decrease of corrosion resistance which is caused by $Cr_{23}C_6$ formation on the grain boundaries. In the presented work corrosion parameters of the modified elements was investigated. The substrate material used in this work was AISI 316L stainless steel. The hybrid process was performed by RF PACVD method and consisted in carburizing of the sample at the beginning and afterwards carbon film synthesis. The corrosion resistance investigation was conducted using saline solution at similar to human body temperature (37°C), the duration of the investigation was two weeks. Corrosion investigation of modified elements proved that suitable choice of carburizing parameters during the hybrid process doesn't cause lowering of corrosion resistance of AISI 316L steel. Moreover microscope observations of the modified materials' structures didn't show any track of carbide disengagements on the grain boundaries.

Keywords: hybrid carbon layer, corrosion resistance of stainless steel, RF PACVD methods

[Engineering of Biomaterials, 76, (2008), 20-23]

Introduction

Carbon coatings, allowing on airtight covering of modified element surface, improve the properties (high hardness, good corrosion and wear resistance, good adhesion, effective thermal conductivity and high biocompatibility) of treated elements and have found applications in orthopaedics, cardiovascular components, guidewires, etc [1]. However, as the carbon coatings are very thin, when they are coated on soft material like austenitic stainless steel, they can flake off. That is caused by plastic deformation under high load [2,3]. The only way to avoid this kind of damage is the substratum hardening, what is possible due to the carburizing of the material. However, carburizing of the element made of the austenitic stainless steel is connected with reduction of its corrosion resistance caused by long influence of temperature above 550°C (above this temperature the chromium carbides ($Cr_{23}C_6$) are formed on the grain boundaries) [4]. In recent years the low-temperature carburizing is very popular for stainless steel, because of the only 470°C process temperature.

Cao et al. proved that during the carburizing process carried out in low temperature there are only Hägg carbides - Fe_3C_2 in the material [5-7].

Ueda et al. described duplex treatment of AISI 304 austenitic stainless steel, but it was carried out with use of two separated equipment: for the DC power source apparatus carburizing process, whereas manufacturing of DLC coating was realized with use of RF plasma CVD method [3]. Authors of presented work carburized and then coated the AISI 316L stainless steel in one two stages process inside the RF PACVD reactor chamber. The corrosion investigation proved that good assorted parameters of hybrid process do not cause reduction of corrosion resistance.

Materials and methods

As a substrate material the AISI 316L stainless steel was used. The stainless steel bars of 20mm diameter were cut into 6mm pieces. The faces of the discs were ground.

The hybrid was made during one process consists of two stages, inside the RF PACVD reactor chamber with use of different reactive mixtures depending on the process stage. First stage consisted in manufacturing of the diffusive layer and it was carried out in the flow of two gas mixtures: $Ar+H_2+CH_4$ or $Ar+CH_4$, in the second stage the adhesive carbon layer was deposited using the CH_4 . The parameters of the process are presented in TABLE 1.

TABLE 1. Parameters of hybrid process.

	RF Carburizing process		Carbon layer manufacturing	
	etching	process	etching	process
Time [min]	30	150 - 300	10	3
Gas mixture	$Ar+H_2$, -	$Ar+CH_4$, $Ar+H_2+CH_4$	-	CH_4
Potential [V]	800	600 - 1000	1000	800

The corrosion resistance investigation was conducted using device showed on FIGURE 1. Investigated sample was dipped in saline solution at similar to human body temperature (37°C). The constant temperature was kept with thermostat. The duration of the investigation was one or two weeks, depending on the corrosion growth.

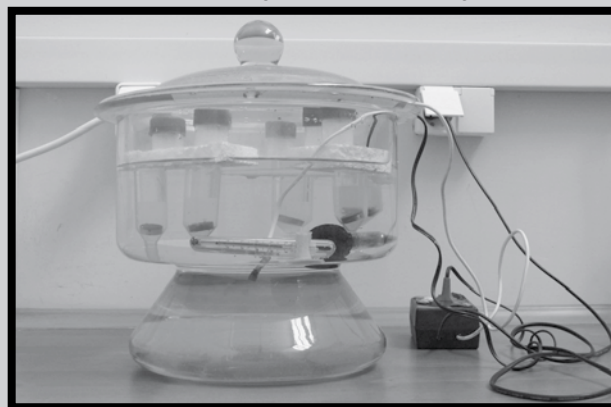


FIG. 1. Device use to corrosion resistance investigation at similar to human body temperature.

The microstructures of treated layers were observed with a scanning electron microscopy (SEM) after etching with use of a solution composed of 10 ml of nitric acid, 20 ml of hydrofluoric acid and 30 ml of glycerine. A sample surface after the corrosion test was investigated using the optical microscopy.

Results and Discussions

Influence of the process parameters on the materials structure

Diffusive layer in the material

On FIG. 2 are showed the cross sectionals micrographs of the modified AISI 316L stainless steel samples after etching. On some of the photos (a,b,c) man can obtain tracks of the grains fragmentation in the material. These are the thickest (45 μm) and the best visible on the picture 2b because the sample was etched by 30 minutes at 1000V and then carburized by 5 hour at 1000V. Picture 2a shows the grains fragmentation reach the depth of 6 μm .

Good visible carburized layer show pictures 2e and 2f. The thickness of this layers amounts 3 μm and 2,5 μm accordingly. Sample 5 was heated by 30 minutes and then carburized with use of $\text{Ar}+\text{H}_2+\text{CH}_4$ mixture by 5 hours, sample 6 was not heated and was carburized with use of $\text{Ar}+\text{CH}_4$ by 5 hour. The carburized layer is not visible in sample 4, which was etched by 30 minutes in $\text{Ar}+\text{H}_2$ mixture and then carburized by 5 hour in $\text{Ar}+\text{H}_2+\text{CH}_4$.

Adhesive carbon films on the material surface

Picture 2a shows 2 μm thick adhesive film on the sample surface, but in some places the layer tears off the surface. On the pictures 2a and 2c the carbon layer is very thin. The adhesive films of above – mentioned samples were manufactured the same day as the carburizing process. The authors think that it is the reason of the grains fragmentation in the material.

There is a thick layer on the sample surface on d (2 μm) and e (3 μm) picture, but this layer isn't strongly coherent. The 0,5 μm thin layer but good coherent is showed on picture f. The adhesive layer, of the sample number 4,5 and 6 samples was produced the next day after slow cooling of the sample inside the reactor chamber. The authors think that it is the reason why the grains fragmentation inside the material in this case is not visible.

FIG. 2. Cross section of the treated sample:
a) sample no 1; b) sample no 2; c) sample no 3;
d) sample no 4; e) sample no 5; f) sample no 6.

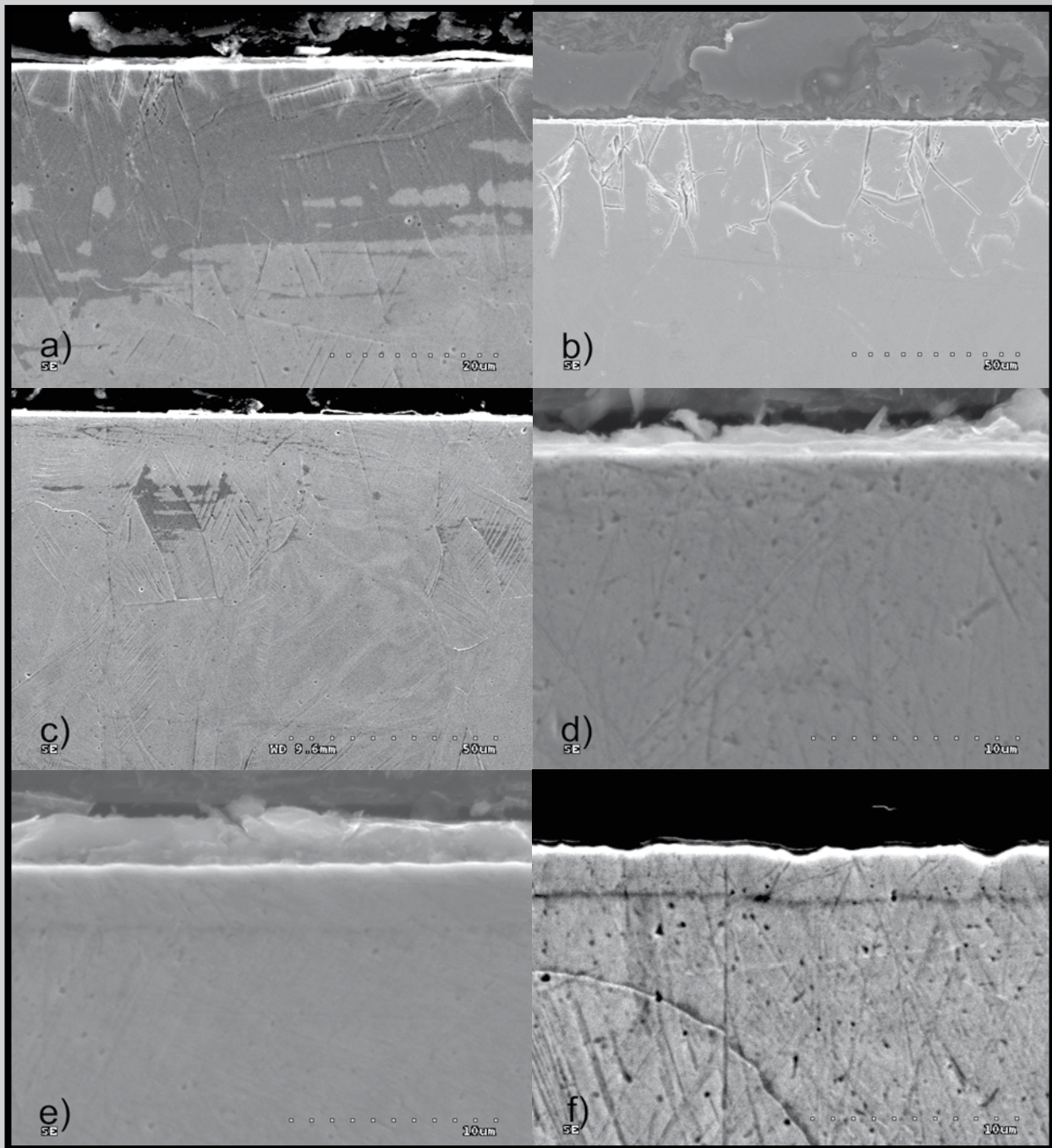


TABLE 2. Saline immersion test result.

No	Immersion time			
	1h	24h	One week	Two weeks
1	Slightly yellow liquid	Insignificant amount of corrosion products in test-tube	Numerous small pits – investigation was stopped	-
2	Intensive yellow liquid colour	A lots of corrosion products in test-tube	Pits on the whole sample's surface – investigation was stopped	-
3	Liquid colour without alteration	Slightly yellow liquid, very little of corrosion products	A little of small pits on the sample surface – investigation was stopped	-
4	Liquid colour without alteration	Liquid colour without alteration	Liquid colour without alteration	Liquid colour without alteration, layer separations were visible
5	Liquid colour without alteration	Liquid colour without alteration	Liquid colour without alteration	Liquid colour without alteration
6	Liquid colour without alteration	Liquid colour without alteration	Liquid colour without alteration	Liquid colour without alteration

Influence of the process parameters on the corrosion properties

Observation of liquid colour

An observation of the liquid's colours and surface facies of the samples during the one or two weeks-long corrosion test was carried out. The duration of the test was depended on the corrosion progress, if there was an intensively yellow liquid and a lot of corrosion products in the test – tube, the test was stopped. The results of the observation are presented in TABLE 2. In case of sample 2 there was well visible change of liquid's colour after one hour incubation in the saline solution and after one day there were a lot of corrosion products in the test - tube. The investigation was discontinued after one week and on the sample surface were observed good visible pits. The examination was stopped after one week also in case of the samples 1 and 3, for the sake of changes in liquid colours and a few pits on the surface. Without colour changes of was saline solution being in contact with the samples 4, 5 and 6 after two weeks of incubation. After this time there were visible layer separations on the 4th sample surface.

The microscopic observation confirmed the macroscopic observation. There were well visible pits on the surface of samples number 1, 2 and 3 after one week long corrosion test (FIG. 3.). In case of sample 2 the whole surface was covered by rust - coloured pits. Samples 1 and 3 had less of pits but these were also good visible. The authors think that the high bias voltage and long time of the hybrid process causes the grains fragmentation in the material. Furthermore, it is considered that the high bias voltage causes the material's overheating and contributes to the chromium carbides formation on the grains boundaries, what is responsible for the reduction of corrosion resistance.

The microscopic observation of the samples 4, 5 and 6 didn't show any pits on the surface (FIG. 4.). It is thought that the reason of the better corrosion resistance of these samples is the fact that the carbon layer was manufactured next day after slow cooling of the sample inside reactor chamber. The visible layer separation was visible only in case of sample 4 and 5. On the surface of sample number 6 no were observed. The authors think that the essential influence on the layer separation has the surface preparation.

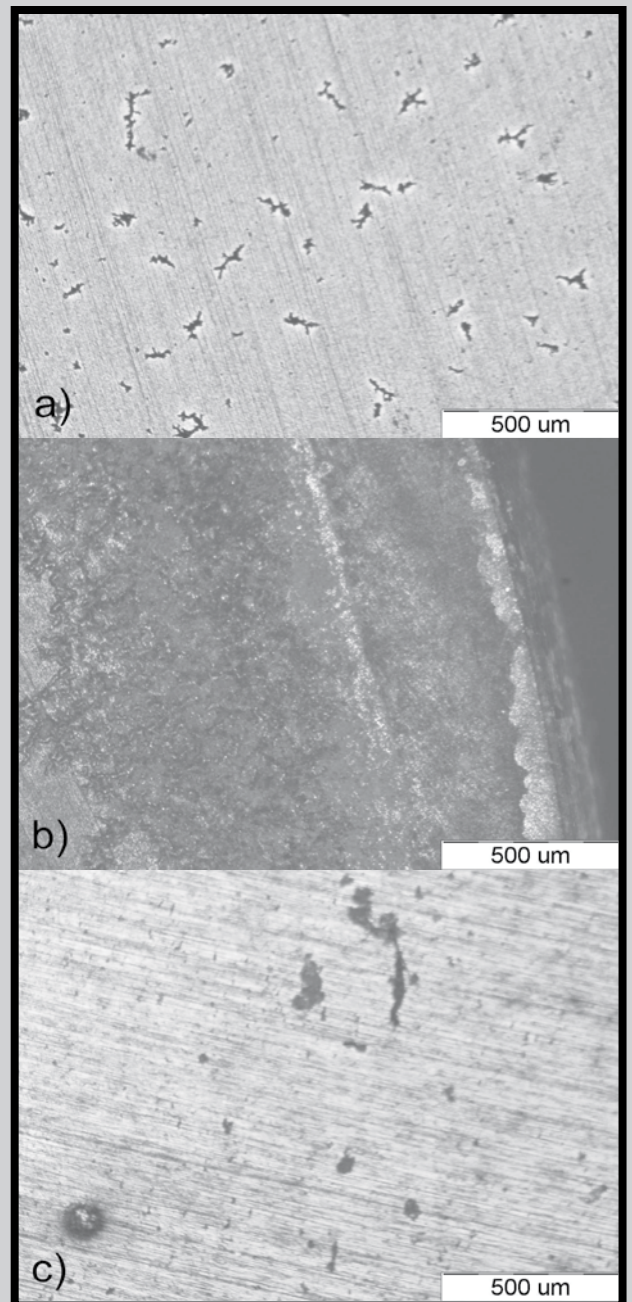


FIG. 3. Microphotographs of AISI 316L stainless steel surface treated in hybrid RF PACVD process after one week long corrosion test: a) sample no 1; b) sample no 2; c) sample no 3.

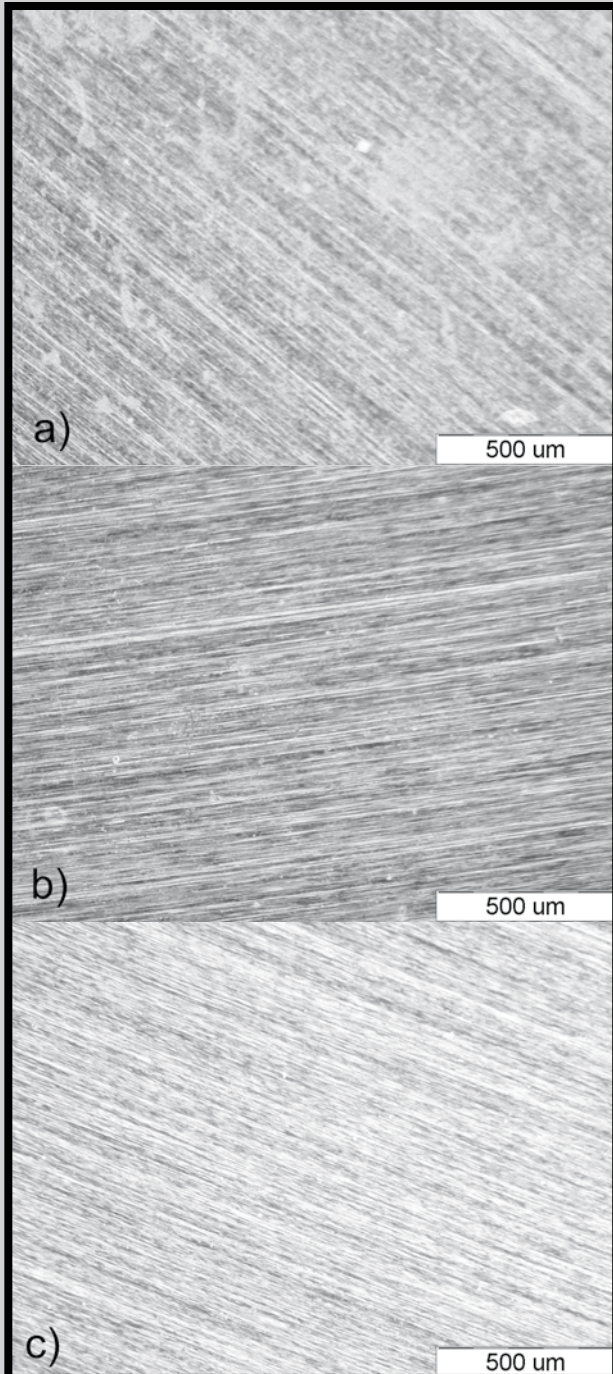


FIG. 4. Microphotographs of AISI 316L stainless steel surface treated in hybrid RF PACVD process after two weeks long corrosion test: a) sample no 4; b) sample no 5; c) sample no 6.

Conclusions

Conventional carburizing process of elements, which are made of austenitic stainless steel, can induce their damage. This endamage is created by lowering of the corrosion resistance. The authors proved that it is possible to manufacture the hybrid layer with use of RF PACVD method on the AISI 316L stainless steel without reduction of their corrosion resistance. The SEM investigation demonstrates, that the hybrid process allows to manufacture the carburized layer of 2,5 to 3 μm thickness, whereas the carbon layer on the surface was in range of 0,5 to 3 μm thick. Corrosion investigations performed with use of saline solution proved that elements, modified in hybrid process with well – chosen parameters, didn't lose their corrosion resistance.

Acknowledgments

This work was financed by the Polish State Committee in 2007-2009 for Scientific Research No N N507 4469 33.

References

- [1] Geoffrey Dearnaley, James H. Arps: "Biomedical applications of diamond-like carbon (DLC) coatings: A review", *Surface and Coatings Technology*, No. 200, 2005, pp 2518-2524.
- [2] Jun Qu, Peter J. Blau, Brian C. Jolly: "Tribological properties of stainless steels treated by colossal carbon supersaturation", *Wears*, No. 263, 2007, pp 719-726.
- [3] N. Ueda, N. Yamauchi, T. Sone, A. Okamoto, M. Tsujikawa: "DLC coating on plasma – carburized austenitic stainless steel", *Surface and Coatings Technology*, No. 201, 2007, pp 5487-5492.
- [4] Bong-Seok Suh, Won-Jong Lee: "Surface hardening of AISI 316L stainless steel using plasma carburizing", *Thin Solid Films*, No. 295, 997, pp 185-192.
- [5] Y. Cao, F. Erns, G.M. Michal: "Colossal carbon supersaturation in austenitic stainless steels carburized at low temperature", *Acta Materialia*, No. 51, 2003, pp 4171-4181.
- [6] F. Ernst, Y. Cao, G.M. Michal: "Carbides in low-temperature-carburized stainless steel", *Acta Materialia*, No. 52, 2004, pp 1469-1477.
- [7] G.M. Michal, F. Ernst, H. Kahn, Y. Cao, F. Oba, N. Agarwal, A.H. Heuer: "Carbon supersaturation due to paraequilibrium carburization: Stainless steels with greatly improved mechanical properties", *Acta Materialia*, No. 54, 2006, pp 1597-1606.