GAZİOSMANPAŞA BİLİMSEL ARAŞTIRMA DERGİSİ (GBAD)
Gaziosmanpasa Journal of Scientific Research
ISSN: 2146-8168
http://dergipark.gov.tr/gbad
Review Article(Derleme Makalesi)

Cilt/Volume : 12
Sayı/Number: 2
Yıl/Year: 2023
Sayfa/Pages: 57-72

***Alınış tarihi (Received)*:** 25.05.2023
***Kabul tarihi (Accepted)*:** 10.07.2023

Corrosion Resistance Of Diamond Like Carbon (DLC) Coatings In The Biomedical Field

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ABSTRACT: Biomaterials play an important role in the human body. However, they have a tendency to corrode due to the environmental conditions they are exposed to inside the body. For this reason, there is a need to improve the corrosion resistance of biomaterials for the longevity of implants used in the body. Surface coating applications offer an important solution in this field. Today, diamond carbon coatings (DLC) are gaining importance in the biomedical field. The most important features of this coating are its high corrosion resistance and good adhesion to the surface in order to fulfill the expected functions. At the same time, DLC coatings used in biomaterials can work biocompatible with living tissues. In this review, the corrosion behavior of DLC coatings obtained by using the PVD (Physical Vapor Deposition) method was investigated.

Keywords*- DLC Coating, Corrosion, PVD method*

Biyomedikal Alanda Elmas Karbon (DLC) Kaplamaların Korozyon Direnci

ÖZET: Biyomalzemeler insan vücudunda önemli görevler üstlenmektedir. Ancak vücut içinde maruz kaldıkları ortam şartları sebebiyle korozyona uğrama eğilimleri vardır. Bu nedenle vücutta kullanılan implantların uzun ömürlü olmaları için biyomalzemelerin korozyon direncinin iyileştirilmesine ihtiyaç vardır. Yüzey kaplama uygulamaları bu alanda önemli çözüm sunmaktadır. Günümüzde biyomedikal alanda elmas karbon kaplamalar (DLC) önem kazanmaktadır. Bu kaplamanın en önemli özellikleri korozyon direncinin yüksek olması ve kendinden beklenen fonksiyonları yerine getirmesi için yüzeye iyi yapışma kabiliyetidir. Aynı zamanda biyomalzemelerde kullanılan DLC kaplamalar canlı dokularla biyouyumlu çalışabilir. Bu derlemede, PVD (Fiziksel Buhar Biriktirme) metodu kullanılarak elde edilen DLC kaplamaların korozyona karşı davranışları incelenmiştir.

Anahtar kelimler*- DLC Kaplama, Korozyon, PVD metodu*

1. Introduction

Corrosion occurs as a result of the chemical or electrochemical reaction of metallic materials with the effect of the environment (Özkömür, 2008). The driving force of the corrosion phenomenon is the tendency of metals to return to their stable state in nature (Kaya and Asan, 2006). The corrosion behavior of the materials that work in the biomedical field is very important (Sharma and et al., 2008). Stainless steels of the iron-based alloy class is chosen because they resist corrosion. The type of steel contains a certain amount of important Cr element. It should also contain at least one different element such as nickel (Ni), molybdenum (Mo), manganese (Mn), nitrogen (N), etc(Köse, C., 2016; Zaffora, Di Franco, and Santamaria, 2021). Nowadays, metal implants with high mechanical strength and corrosion resistance are used in the repair of bones in healthcare (Stango, Karthick, and et al., 2018). Metal implants also have some disadvantages for living tissue. Due to the release of metal ions such as Ni and Cr from stainless steel into the body fluid, the implant becomes susceptible to corrosion. Corrosion-resistant stainless steel contains more than 12 wt% Cr element. This is because Cr forms a passive chromium oxide (Cr_2O_3) layer on the surface of the alloy, thanks to its passivation property. As a result, this thin oxide layer protects stainless steel from corrosion. Ni and Mo can be added if it is desired to increase corrosion resistance (Köse and Kaçar, 2016; Köse, Kaçar, Zorba, and et al., 2016; Khan, S.A, Shahid, S., and et al., 2021). Microstructures of austenitic stainless steels have better weldability than martensitic and ferritic stainless steel series (Köse, C., 2016). In the biological environment, the implants subjected to regular and cyclic loads exhibit mechanical weakness due to corrosion and bending. In addition, the cells form strong oxidation and enzymes cause corrosion in the implant material (Danışman, Savaş and et al., 2008).

Corrosion factors in the body are temperature changes, interaction with continuous body fluids, pH changes caused by food in the mouth, oxygen pressure changes, mechanical forces. Orthopedic implants and dental prostheses are used instead of hard tissue. Metallic biomaterials have good mechanical properties and are generally preferred for hard tissue replacement implants. Biocompatibility in metal implants is also important in terms of corrosion resistance in the body (in vivo environment). As a result of this corrosion products can enter the tissue and harm the cells. Therefore, biomaterials which are used in vivo should be tested in serum, saliva and different synthetic buffer solutions (Dalibon and et al., 2017; Danışman and Teber, 2016). At the present time, AISI 316L implant stainless steel is used more in healthcare. Approximately alloy elements in the chemical structure of AISI 316L austenitic stainless steel; 2% Mo, 19% Cr, and 12-14% Ni (Azhar Mohammada, and et al., 2013). The thin protective Cr_2O_3 layer formed on the surface of field of use, which has good biocompatibility and strength, provides corrosion resistance. It is used in orthodontic wire, orthopedic implants and cardiovascular stents. (Köse and Kaçar, 2016; Köse, Kaçar, Zorba, and et al., 2016; Köse, 2016). AISI 420 martensitic stainless steels are used in orthopedic manufacturing such as artificial knee joint components, tools and apparatus due to their good mechanical properties and corrosion resistance (Köse, 2016, Köse, 2018). AISI 2205 duplex stainless steel (DSS) has two phases, ferrite (α) and austenite (γ). Its Ni content is lower than that of austenitic stainless steel, making it a suitable material in the human body. AISI 2205 steel has high strength and corrosion resistance (Hammood, and et al., 2019). This steel, containing 22% Cr, 5-6% Ni and 3% Mo, N-alloyed is duplex stainless steel. (Köse, Kaçar, Zorba, and et al., 2018). Implants used in the body should not cause toxic reactions in their biological structure and should be compatible in case of contact with blood (Bociaga and et al., 2017). Numerous clinical symptoms have been reported about ion release due to corrosion in metallic materials (Özkömür, 2008). Over the last few decades, the use of metallic biomaterials in medical implants has increased (Matusiewicz and Richter, 2022). By using PVD method at 550°C for 6 hours, medical grade CoCrMo alloy was coated with titanium nitride (TiN). In addition, potentiodynamic polarization tests confirmed that Ti protection from corrosion was enhanced with TiN. This reduced release of metal ions is attributed to the surface oxide changing to a stable homogeneous rutile TiN structure. (Türkan, and et al., 2006).

The purpose of the coating is to investigate stainless steel biomedical tools treated with ion release and surfaces treated with ions. As a result of the coating, there was approximately

40% reduction in metal surfaces (Browne and Gregson, 2000). More than 95% of known chemical compounds are bond of C chains. C, within a diamond crystal structure, is one of the most famous materials. Diamond, one of the best-known allotropes, is a hard and insulator. C, within a graphite amorphous structure, is very smooth, conductive, and lubricant. Fig. 1 lists major known allotropic forms of C, its selected properties and availability (Falcao and Wudl, 2007; URL-1, 2023; URL-2, 2023).

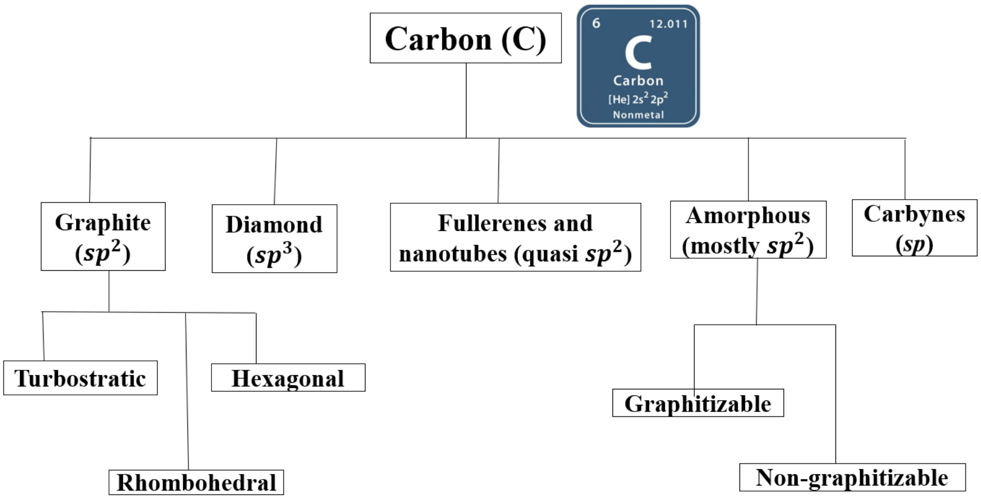


Fig. 1. Allotropes of C (Falcao and Wudl, 2007; URL-1, 2023; URL-2, 2023)

DLC (Diamond Like Carbon) coating has a C structure with interesting properties that compete with crystal structures such as diamond and graphite. For this reason, the usage of DLC coating in biomedical applications has become an attractive focus for researchers in recent years (Danışman, Çelebi, Danışman, Bıçakcı, 2022). In the biomedical category mainly has been include DLC coatings; It is used as a surface corrosion protector in surgical implants in order to increase the wear resistance in orthopedic implants (Danışman, 2017). DLC coatings have a feature to prevent the dissolution of metallic ions in the body. Depending on the coating process and parameters, the sp^3/sp^2 ratio can control the properties of the coating such as hardness, abrasion resistance, friction coefficient, chemical stability (Kurt, 2006). DLC, combining these two different diamond and graphite properties therefore have high hardness levels - in the range of classical tribological PVD coatings (vickers hardness; 1500 - 3200 HV) (Fig. 2) (Kosarieh et al, 2016; URL-3, 2023).

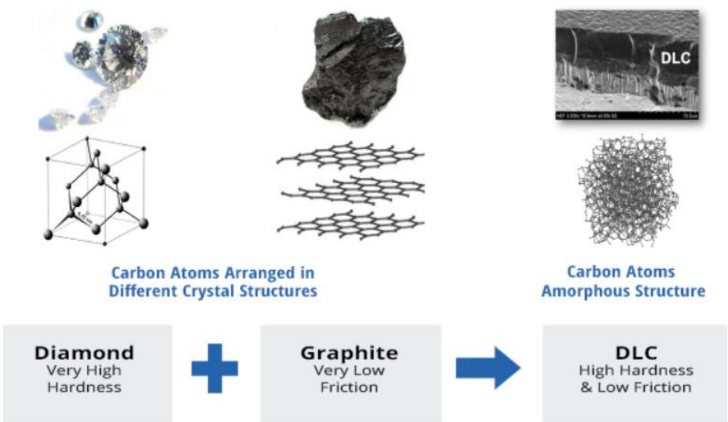
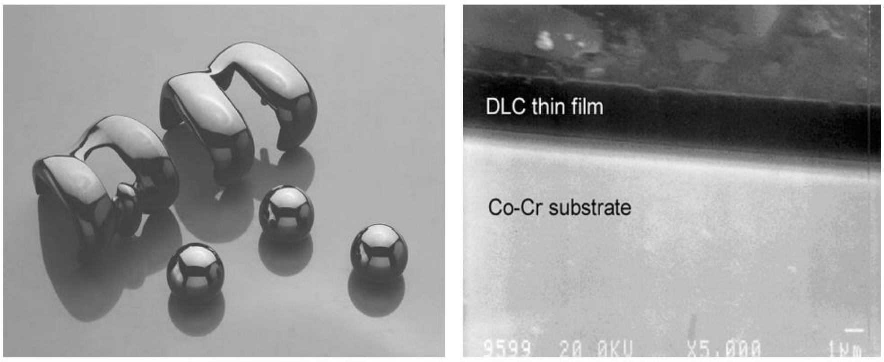


Fig. 2. Types of C molecular bonds (Kosarieh et al, 2016; URL-3, 2023)

DLC coatings are biocompatible coatings with biological stability. Additives are used in biomedical applications to significantly enhance the properties of DLC coatings. The material that has a positive effect on the mechanical properties and corrosion resistance of DLC coatings is silicon. Si-doped DLC coating samples produced by DC-RF magnetron sputter coating method are promising in biomedical applications (Bociaga and et al., 2017). There are studies reporting that the nickel release caused by corrosion on NiTi wires used in the orthodontics treatment is prevented by DLC coating application (Özkömür, 2008). Fibroblastic cells are not cytotoxic by plasma-produced DLC coating. DLC coatings were biocompatible in vitro, and in vivo tests are underway (Uzumaki and et al., 2006). It has been determined that the materials of choice for joint prosthetics are austenitic stainless steel, titanium alloys, zirconium alloys, and Cr-Co alloys In Fig. 3. The synergistic effects due to the ionization intensity that occur during deposition in the plasma environment provide an increase in hardness on the material surface. Plasma-based technologies are expected to benefit both ex vivo and in vivo medical devices (De Las Heras and et al., 2009).



(a) (b)

Fig. 3. (a) DLC coated knee prosthesis (top, left) and femoral heads for hip prosthesis (bottom, right) (b) SEM image of a DLC coating, × 5000 (De Las Heras and et al., 2009)

316L SS, CoCrMo and titanium alloy are widely used biomedical materials in the body. However, these implant materials can release metal debris and ion due to wear and corrosion when working in body fluid. Metal residues and ions can cause tissue inflammation. To avoid this, the recommended DLC coatings can decrease the wear and corrosion of the base materials. In order to achieve this, it is significant that the coating sticks good to the base material and there are many factors such as surface roughness, internal stresses, interface chemical bonds (Zhang and et al., 2015). Stainless steel (SS) and alloys, titanium and its alloys, CoCr and its alloys are widely used as metal materials in hip prostheses. These metal alloys are exposed to metal ionization in the body fluid and cause allergic reactions in the body. DLC coating applications, multi-layer coating applications and ceramic thin film applications on surfaces are gaining importance in order to increase the wear and corrosion resistance of metal alloys and to reduce the release of metal ions on surfaces (Rahaman and et al., 2007; Cui and et al., 2017; Gilewicz and et al., 2016). The hard ceramic coatings produced by using the Physical Vapor Deposition (PVD) method yielded a significant enhance in the corrosion resistance of the Ti6Al4V alloy (Danışman and Teber, 2016). As the deposition time and coating thickness of DLC coatings on the substrate increased, the corrosion resistance of the material also increased. It has been shown that sp^3 bonds in the structure of DLC coating affect the properties such as hardness, chemical and electrochemical corrosion resistance, abrasion and friction (Sharma, Barhari and et al., 2008).

DLC coatings have been shown to prevent cytotoxicity (cell poisoning) in biomedical materials, and the extraordinarily intense structure of DLC against corrosion media enhances biocompatibility. DLC coatings can provide solutions as protective coating in biomedical applications to prevent corrosion. In this study, the effects of the PVD method on corrosion behavior of DLC coatings were investigated in the literature.

2. Physical Vapor Deposition Method

PVD coating method is carried out in a vacuum environment and has two basic methods: evaporation and sputtering. Depending on the resources used in these methods, they are subdivided into subclasses. Today, the most commonly used methods are cathodic arc evaporation with high deposition rates, magnification by ion beam and magnetic sputtering. These methods are performed in the plasma (ionized gas medium) obtained in the vacuum environment. Different coating types can be formed by using different gases in the working environment (Danışman and Teber, 2016). PVD technology is a method in which atomic thin film deposition occurs on the surface of a material. PVD is a physics-thermal collision process that transforms the material to be deposited. The ionised particles are oriented on the substrate through the application of a potential. In Fig. 4 (a and b), arc deposition; the target can act as either a cathode (cathode arc) or an anode (anode arc), depending on its type and the coating to be obtained (Michailidis and Bouzakis, 2019; URL-2, 2023).

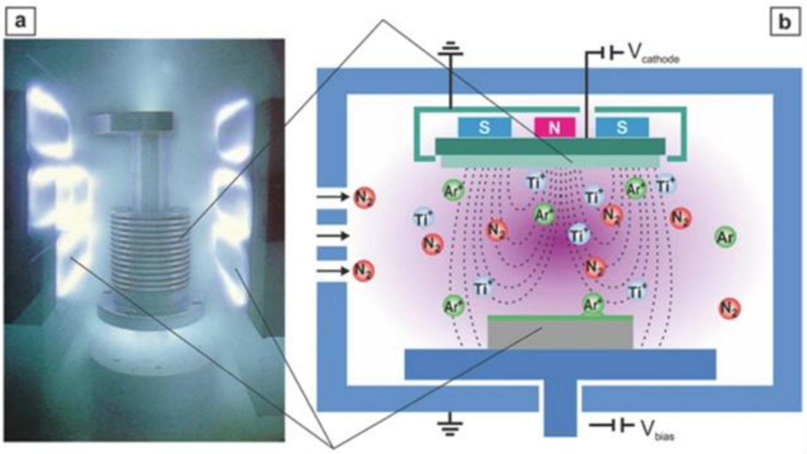


Fig. 4. Arc deposition from PVD coating method (Michailidis and Bouzakis, 2019)

The properties of the DLC coatings can vary depending on the reactive gas pressure and gas concentration. In this method, the thickness of the coating and the surface roughness are proportional to the increase in coating process time. The temperature required for DLC coating with PVD is 250-400°C under ideal conditions and can be applied between 70-450°C. The main advantage of PVD is that it can be done at low temperatures, even at room temperature. The thickness of the formed film is 2-5 microns. The basic problems encountered with PVD thin coatings are related to surface roughness and film density. The coefficients of thermal expansion of the base metal and the coating layer must be compatible (Karabağlar, 2015). DLC coatings obtained by the unbalanced magnetron sputtering method in the closed area provide a dense plasma in the base material region, which increases the ion bombardment of the growing film. DLC coatings obtained by this method have good corrosion resistance. The distance between the target and the substrate affects the ionization rate and the formation of the film on the surface (Kurt, 2006). Multi-layer DLC coating applications are performed by a magnetron sputtering method. It is seen that multilayer DLC coatings increase corrosion resistance in salty environments even in seawater (Yea and et al., 2017). A silicon (Si)-targeted DC-RF magnetron sputtering technique is used to obtain Si-DLC coatings. The amount of silicon in Si-DLC coatings affects the adhesion of the coatings. The DC-RF magnetron sputtering method, in which Si-DLC coatings are obtained, is assuring method for biomedical implementations (Bociaga, and et al., 2017).

3. Corrosion Behavior of DLC Coatings

It is often used electrochemical technologies like potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) to estimate the corrosion properties of DLC coatings on metal surfaces. In addition, there are corrosion studies conducted with salt fog tests. The effect of DLC coating on the corrosion behavior of AISI 316L austenitic stainless steel, one of the basic materials in the biomedical field, was investigated by salt fog test. Nitrided austenitic stainless steel (duplex sample) and unnitrided austenitic stainless steel (coated sample) materials were used as substrates for DLC coating. When the 3.5% NaCl test was applied to the coated duplex samples (DLC soft coating + nitrided layer), current density was observed at high potentials. This showed that the duplex was corrosion resistant. The corrosion resistance of duplex coatings is better than coated samples. The results after the salt fog test given in Figure 5 revealed that the DLC coating acted as a good corrosion barrier in the duplex DLC coated sample. In the potentiostatic tests in NaCl solution, it was observed that the defects on the behavior of the DLC film affect the corrosion resistance (Dalibón and et al., 2017).

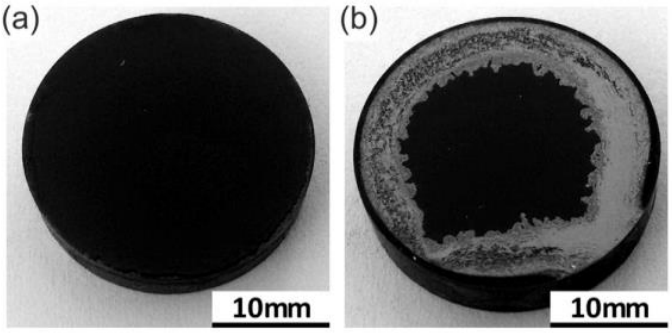


Fig. 5. Corrosion test of DLC coating: (a) Duplex sample, (b) coated sample. (Dalibón and et al., 2017)

Compared to the additive-free pure DLC coating, the Si-DLC coating type has increased the corrosion protection performance. It has been shown that the Si contribution rate improves the corrosion resistance when it increases from 20% to 30% (Choi, Nakao and et al., 2007). Another additive applied to DLC coatings is titanium. Si-doped DLC coatings compared to DLC coatings with Ti additive Si-doped shows superior properties in terms of corrosion resistance (Masami, Setsuo and et al., 2009). A DLC film deposited on AZ31 (Mg–3%Al–1%Zn) showed anticorrosion properties (Fig. 6 (a and b)). Plasma-based ion implantation and deposition (PBII&D) was used to deposit DLC and Si–DLC films on sputter. 0.05 M NaCl electrolyte solution was used for recording potentiodynamic polarization curves. With increasing Si content in DLC films, corrosion protection performance improved, and Si incorporation further improved corrosion protection. Si–DLC coatings become less cracked and pitted (Fig. 6 (c and d)), resulting in low corrosion currents and higher corrosion potentials. Si-doped DLC coating on magnesium alloy has enhanced corrosion protection. AZ31 film corrosion performance was improved thanks to the oxygen plasma treatment which formed a magnesium oxide layer on the film and increased electrical resistivity. DLC coatings made after this pre-treatment significantly increased the corrosion performance of the magnesium alloy (Fig. 6) (Choi and et al., 2007).

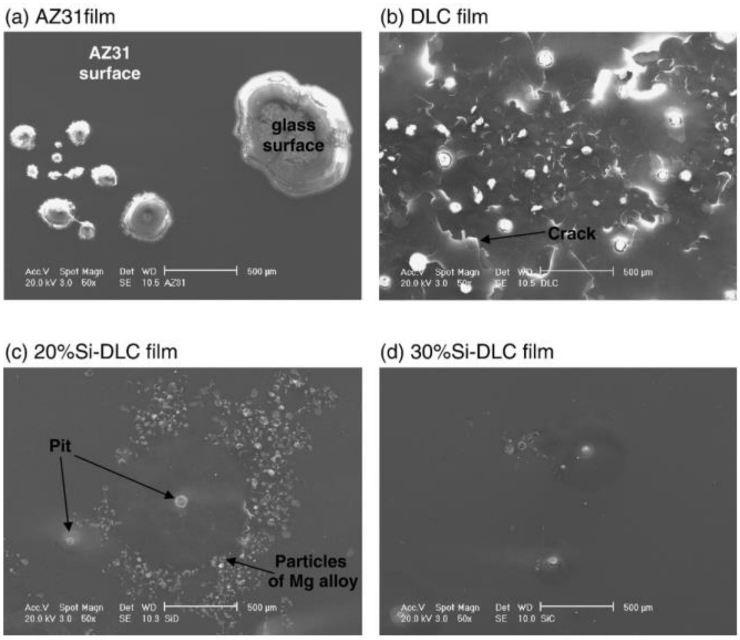


Fig. 6. Sample surfaces after corrosion tests (SEM) (Choi and et al., 2007)

The corrosion resistance of DLC coatings performed on 316L SS, CoCrMo, and Ti6Al4V substrates using a filtered cathode vacuum arc (FCVA) coating method was investigated at 37°C in 0.9% NaCl solution and DLC-coated ones showed a very high corrosion resistance compared to uncoated ones. When the results of the dynamic polarization test are examined; all DLC-coated samples were found to have higher corrosion potential and lower current. After coating, the potential value of the Ti6Al4V alloy (-0.266V) increased to (-0.039V). The others changed from (-0.036V) to CoCrMo alloy (-0.225V), from 316L SS (-0.148V) to (-0.033V), respectively. DLC coatings can successfully defend metal substrates and reduce corrosion rate. The lowest current value is also observed in the DLC-coated Ti6Al4V alloy. The stability of the coated Ti6Al4V alloy is higher than the other two base materials, indicates that corrosion protection is more effective (Zhang et al., 2015).

Hydrogen doped amorphous carbon (a-C: H) coatings can be classified as soft or hard depending on sp^3 bonds, hydrogen content and hardness. These as-deposited DLC coatings are characterized by low friction coefficient, chemical stability and abrasion resistance. For as-deposited DLC coated specimens, the corrosion potential and corrosion current of 316L/DLC (-0.033 V, 1.20E-9 A/cm^2), CoCrMo/DLC (-0.036 V, 1.08E-9 A/cm^2) and Ti6Al4V/DLC (-0.039 V, 8.62E-10 A/cm^2) are similar. After 90 days of corrosion test, the corrosion current of all immersed DLC-coated samples was large (Figure 7 (a,b,c)). The corrosion current of Ti6Al4V/DLC increases slightly from 8.62E-10 A/cm^2 to 1.05E-9 A/cm^2, while the corrosion currents of immersed 316L/DLC and CoCrMo/DLC are twice as large. Ti6Al4V/DLC was the best resistant material in the static immersion test. Titanium alloys have better adhesion to DLC coatings than stainless steel and CoCrMo alloys. Compared with the bare metal substrates, all the as-deposited DLC samples reveal a higher corrosion potential and a lower corrosion current. That means DLC coating can successfully protect the metal substrate and lower the corrosion rate. Testing shows that DLC coatings on

Ti6Al4V substrates have better stability than coatings on 316L stainless steel and CoCrMo alloys (Fig. 7) (Dalibon at et al., 2017).

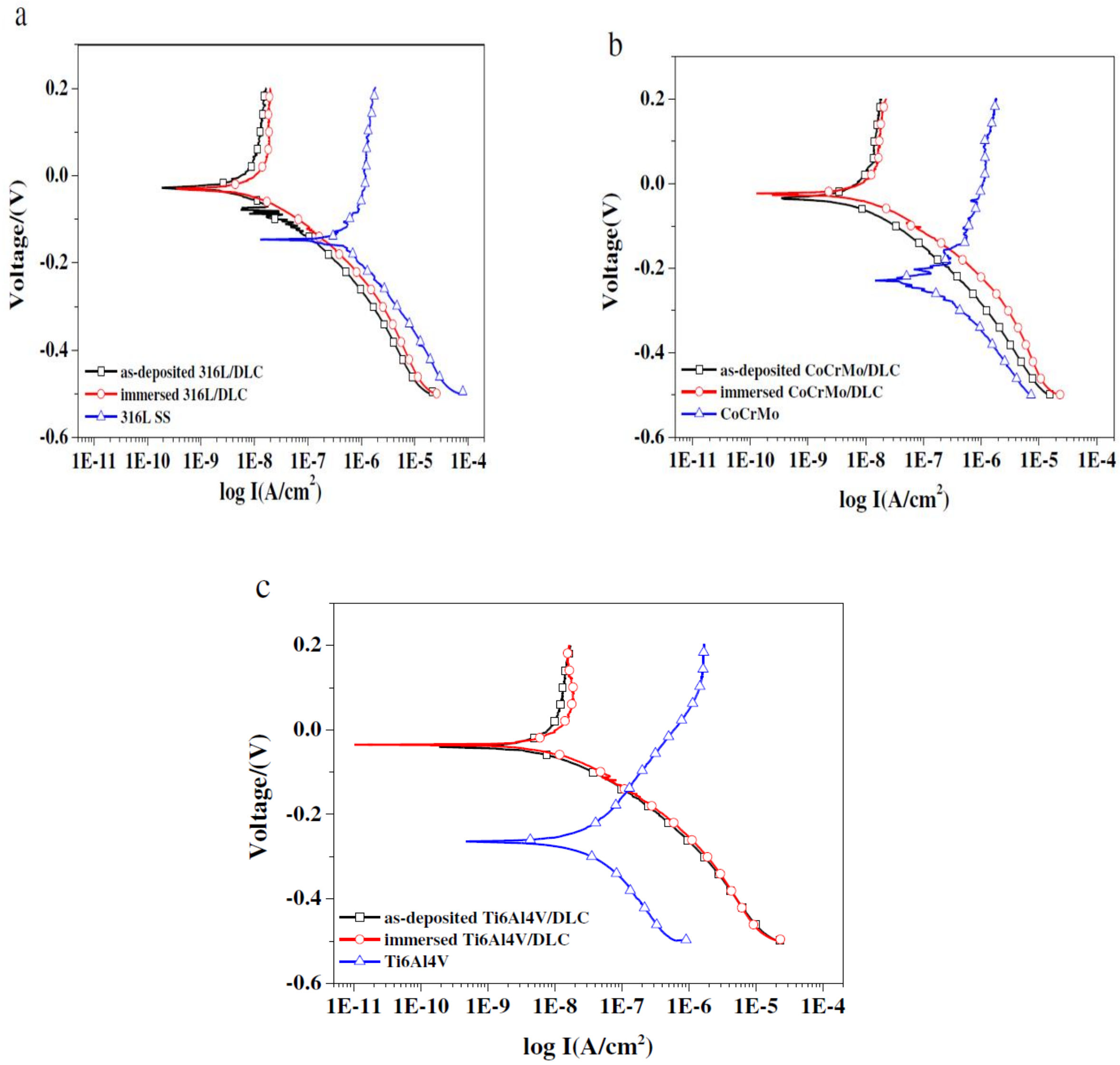


Fig. 7. The bare, as-deposited and immersed DLC-coated samples is Dynamic polarization curves: (a) 316L/DLC, (b) CoCrMo/DLC, (c) Ti6Al4V/DLC (Zhang et al., 2015; Dalibon at et al., 2017)

The corrosion resistance of multi-layer DLC coatings using the unbalanced magnetron sputtering method on 304L SS base material used as biomaterials revealed that the corrosion resistance of 24°C in NaCl solution at room temperature was 20±3°C. When the dynamic polarization test results are examined in Fig. 8, it is observed that the multilayer DLC coatings have high corrosion potential and low current value, thus showing better corrosion resistance of the material. The corrosion potential of uncoated 304L base material is $E_{corr} \cong$ -0.37V and corrosion current density is $I_{corr} \cong 6.39x10^{-5}$ A/cm^2. After applying the multi-layer DLC coating, $E_{corr} \cong$ -0.22 V and $I_{corr} \cong 7.58\times10^{-6}$ A/cm^2 in the same environment. The high corrosion potential and low corrosion current density obtained by the coating reduce the corrosion rate, resulting in better corrosion resistance of the coated base material. Therefore, the corrosion resistance of the multilayer DLC coating appears to have good potential for increased corrosion resistance of the 304L substrate (Sharma and et al., 2008; Yea and et al., 2017).

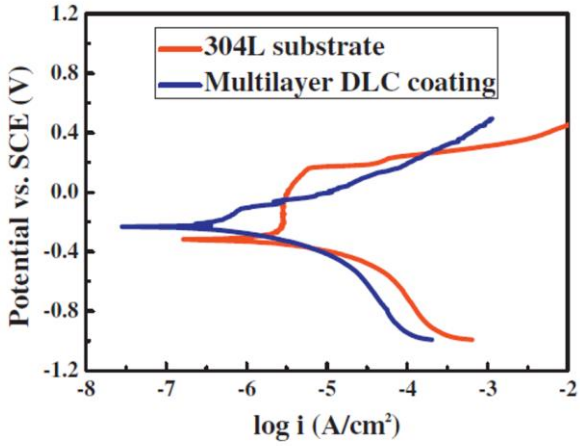


Fig. 8. Corrosion behavior of multi-layer DLC coating during polarization curve of 304L substrate and corrosion tests (Sharma and et al., 2008; Yea and et al., 2017).

316L SS is also used as biomaterial. Firstly, nitriding heat treatment is applied on this steel and then nitride layer is obtained by using unstable magnetic weld sputtering (CFUMBS) method and investigated the effect of duplex operation. The presence of nitrides obtained from the substrate material and the coating interface affected the corrosion resistance of Ti-DLC coated samples. As it is shown in Fig. 9, polarization curves are given for uncoated, nitrided, Ti-DLC coating and duplex surface treated 316L SS samples. When the dynamic polarization test results are examined in Fig. 7, uncoated 316L SS base material (E_{corr} = -83 mV, I_{corr} = 1.50x10^{-4}mAcm^{-2}) value, 316L SS cement material after nitriding at 500ºC for 8 hours (E_{corr} = -340mV, I_{corr} =1.01x10^{-4}mAcm^{-2}), duplex-treated 316L SS base material (E_{corr} = -114mV, I_{corr} = 1.09 x10^{-4}mAcm^{-2}) values were obtained. According to these results, it is observed that the corrosion potential of nitrided samples is lower than the uncoated sample, however, the anodic current densities are also low. After coating with 316L SS base material Ti-DLC (E_{corr} = -19mV, I_{corr} = 8.31 x10^{-5}mAcm^{-2}) was obtained. It is seen that the polarization curve of Ti-DLC thin film coated samples shifts to a higher corrosion potential value and lower corrosion current densities. The polarization curve of nitrided samples showed that the current density was high and the corrosion potential was lower than the uncoated sample. By comparing the polarization curves of Ti-DLC coated and duplex-treated 316L stainless steel, it can be seen that phase formation and surface roughness have a large impact on corrosion resistance. As a result of the Ti-DLC coating, the sample was the most corrosion resistant. This shows that the Ti-DLC coating alone provides good protection (Fig. 9) (Karabağlar, 2015; Yetim, Çelik and et al. 2011).

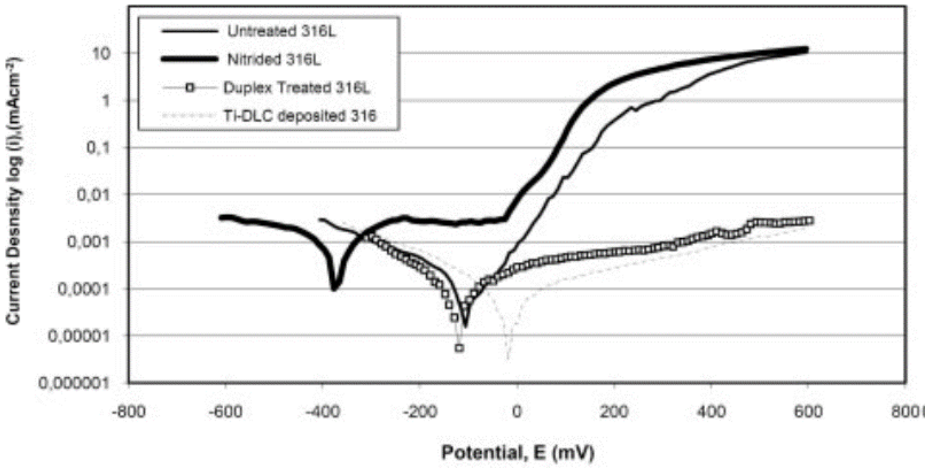


Fig. 9. Current density of 316L SS with different surface treatment curves (Yetim, Çelik and et al. 2011)

As a result of the SEM investigations made on 316L SS base materials treated differently, Pitting corrosion was found to be effective in all samples. In Fig. 10(a), when the surface of the plasma nitrided 316L sample is examined, a large number of pits are observed due to the effect of corrosion. SEM images were seen that in Fig. 10(b) the Ti-DLC deposited 316L specimens did not show defects on the surfaces, such as small pores, and pinholes (Yetim, Çelik and et al., 2011). As a result of the electrolytic cell reaction, the amount of corrosion increased compared to the coated as a result of the homogeneous microstructure, the interaction between the nitrides and the (Yetim, Çelik and et al., 2011, Wua, Zhou and et al., 2018).

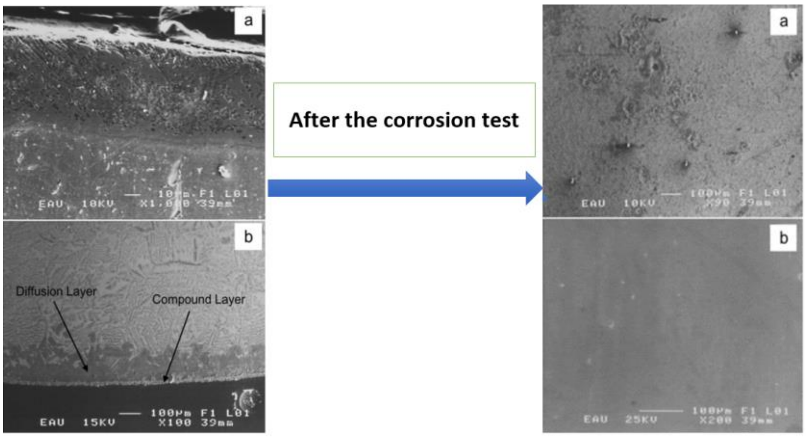


Fig. 10. Corroded surfaces of 316L stainless steel samples is SEM Images (100 µm): a) plasma nitrided, b) Ti-DLC deposited (Yetim, Çelik and et al., 2011).

In Fig. 10(c), duplex treated and nitrided surfaces have similar surfaces when examined. The best corrosion resistance was observed in the Ti-DLC-coated specimens. These results indicated that the Ti-DLC coating is an appropriate surface change for metal implants which are uncoated and nitrided in plasma (Yetim, Çelik and et al. 2011; Wua, Zhou and et al., 2018).

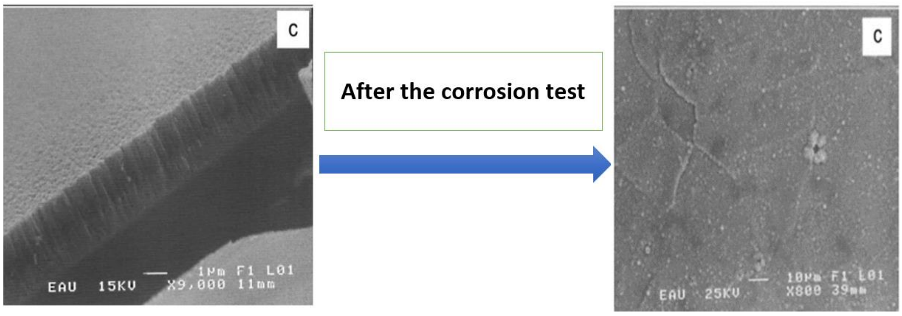


Fig. 10 (continue). Corroded surfaces of 316L stainless steel samples is SEM Images: c) duplex treated (Yetim, Çelik and et al., 2011)

DLC coating was performed by using direct current (DC) reactive magnetron sputtering method on 304 SS base material used as biomaterial. In the case of addition of Ti, Cu and Ce elements as additive-to the DLC coating, the effect on corrosion resistance in the medium containing 3.5% NaCl solution was compared. The Ti-bonded (Cu, Ce)/Ti-DLC coating exhibited a better corrosion resistance than the Ti additive (Cu, Ce) TiDLC coating. The film polarization curves (Cu, Ce)-DLC and (Cu, Ce) / Ti-DLC are shown in Fig. 11. When the test results are examined, the potential range of (Cu, Ce)-DLC coating is from -0.098 to -0.045 V vs SCE (saturated calomelelectrode) and the potential range of (Cu,Ce) / Ti-DLC film is 0.22 to 0.25V vs SCE (saturated calomel electrode) and an anodic peak with potential range. (Cu,Ce)-The anodic peak in the DLC film is observed more clearly than the (Cu, Ce)/Ti-DLC film. (Cu,Ce)-DLC film has higher corrosion current density (I_{corr} = 6.530 x $10^{-7}Acm^{-2}$) and more negative corrosion potential value (E_{corr} = -0.270 V) (Cu, Ce) -DLC film has a worse corrosion protection behavior. The (Cu,Ce)/Ti-DLC film has a lower corrosion current density (I_{corr} = 3.195 x $10^{-8}Acm^{-2}$) and a higher corrosion potential (E_{corr} = -0.137 V). It has better corrosion protection than Ti additive coating. Corrosion media were able to penetrate the film's thin layers and microfractures. Interfacial effect, which prevents the penetration of the abrasive medium into the metal and limits the growth of defects; This is due to the promising corrosion protection property of the (Cu,Ce)/Ti-DLC film (Fig. 11) (Wua, Zhou and et al., 2018).

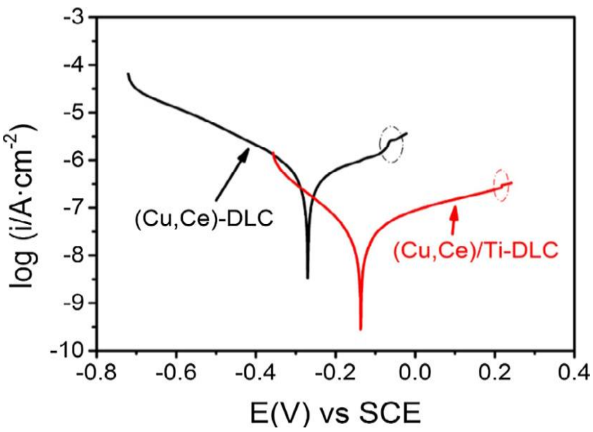


Fig. 11. (Cu, Ce) -DLC and polarization curves of (Cu, Ce) / Ti-DLC films film (Wua, Zhou and et al., 2018)

After the polarization test, for the in-depth analysis, SEM surface surveys of the coatings were made, resulting in pitting corrosion and micro-cracks and pores [19]. When the SEM sample photographs of the (Cu, Ce)-DLC film in Fig. 12 (a and b). Fig. 12(a) was seen before of immersed 3.5% NaCl solution (Cu, Ce)-DLC. Fig 12(b) were examined that surface roughness and pitting corrosion occurred. The SEM photographs of the (Cu,Ce)/Ti-DLC film in Fig. 12 (c and d). Fig. 12(c) was seen before of immersed 3.5% NaCl solution (Cu, Ce)/Ti-DLC film. Fig. 12(d) show that there is no significant damage to the surface after corrosion. It is concluded that the Ti-doped (Cu, Ce)/Ti-DLC film exhibits outstanding anti-corrosion performance (Wua, Zhou and et al., 2018).

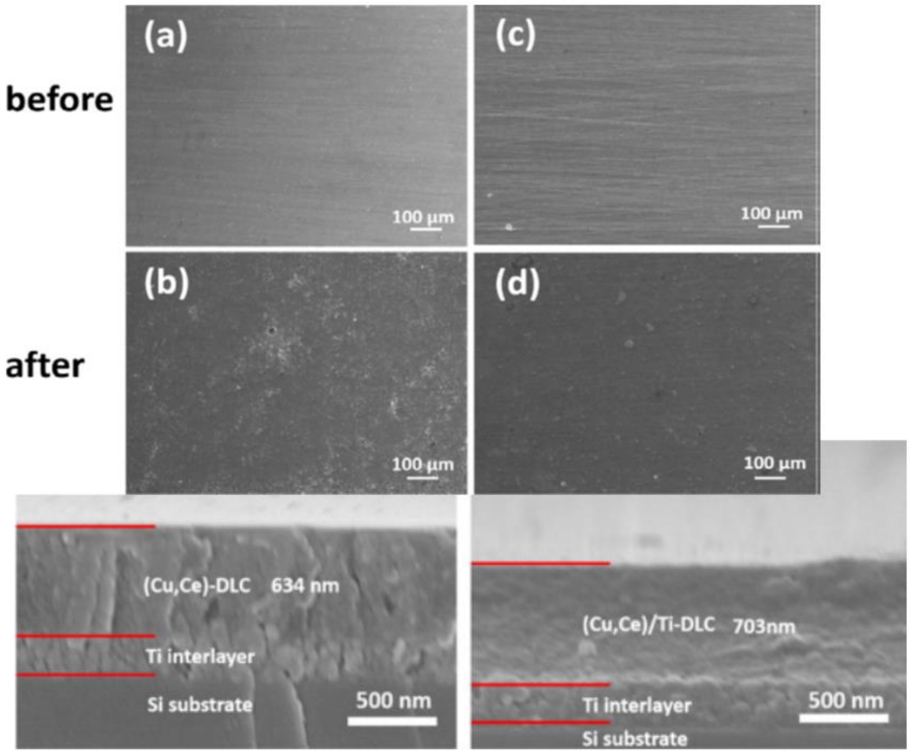


Fig. 12. SEM surface morphologies before and after immersed in 3.5% NaCl solution: (a) before of immersed (Cu, Ce)-DLC, (b) after of immersed (Cu, Ce)-DLC, (c) before of immersed (Cu, Ce)/Ti-DLC (d) after of immersed (Cu, Ce)/Ti-DLC (SEM: 100µm and 500 nm) (Wua, Zhou and et al., 2018)

NiTi alloys are also used as biomedical implant materials. DLC coating was applied to this material by magnetron sputtering method and corrosion behavior was investigated in phosphate buffer solution (PBS). Serum proteins, bovine serum albumin (BSA) and fibrinogen (Fib) were added to phosphate buffer solution for this purpose and the effects of DLC coated NiTi alloy on corrosion behavior were investigated. According to Fig. 13, corrosion current density measured in DLC-coated samples is lower when BSA and fibrinogen are introduced to the solution when polarization curves for coated and uncoated NiTi alloy base materials are removed. The corrosion potential of NiTi alloy base material in PBS was observed to be E_{corr} =-314 mV and the current density was I_{corr} = 4x10^{-6}A/cm^2. The corrosion potential of DLC coated NiTi alloy base material in PBS increased to E_{corr} = -96 mV, and the current density decreased to 2.8x10^{-6} A/cm^2. When the corrosion behavior of the coated sample in the presence of BSA and Fibrinogen is examined; PBS + BSA, the corrosion potential is E_{corr} =-60 mV, current density I_{corr} = 3.5x10^{-6}A/cm^2 PBS + Fib. The corrosion potential in the environment was Ecorr = -83 mV and the current density was I_{corr} = 1.3x10^{-6}A/cm^2. DLC coatings on NiTi alloy reduce current density and increase the corrosion potential in PBS in comparison with uncoated. Corrosion current density measured from DLC, BSA and Fib coated sample when more decreases are present. BSA improves corrosion resistance by covering the pores in the coating. Different layers of coating may affect the adhesion and corrosion resistance of NiTi/DLC system (Fig. 13) (Hang, Chu, 2010).

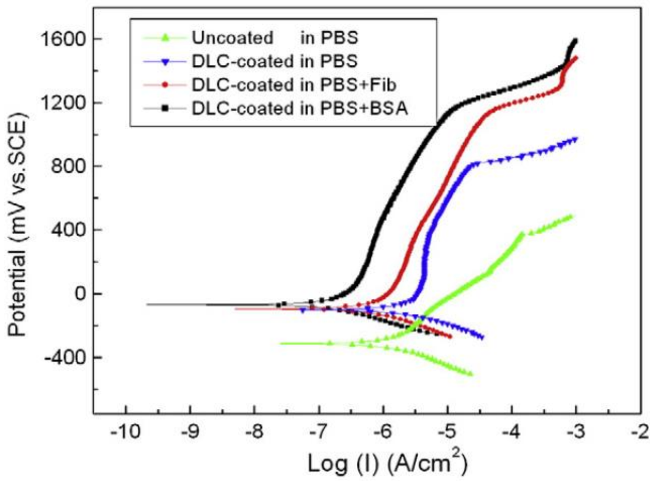


Fig. 13. Uncoated DLC coated NiTi alloy potentiodynamic bias curves in a variety of solutions (Hang, Chu, 2010).

The improvement in corrosion resistance can be attributed to the formation of a passive layer of SiO_x on the surface of the DLC, as the coating becomes increasingly impermeable when Si is added (Zeng and et al., 2002; Lillard and et al., 1997; Papakonstantinou and et al., 2002; Kim and et al., 2005). DLCs with increased silicon content have shown to have improved barrier properties, as indicated by lower current density in the polarization curves as well as higher charge transfer resistance and pore resistance values (Azzi et al., 2010).

4. Conclusion

It is important that the implant materials used in the biomedical area are long-lasting and their duration of use is increased. The coating applications on the implant ensure that the implants are more resistant to corrosion in the body and work more harmoniously with the living tissue without creating any toxic effects. DLC coatings are an effective coating type to increase the corrosion resistance of implant materials. When the potentiodynamic test results of the DLC coatings are investigated, the corrosion potential of the DLC coated base materials is higher and the corrosion currents are lower. Considering that the corrosion current and potential are directly related to the corrosion rate, the corrosion resistance of DLC-coated substrates is shown to be higher than the uncoated base materials and the coating surface provides effective protection against corrosion. When corrosion resistance is examined in different solutions, it is possible to further increase the DLC coating corrosion resistance by addition of additives such as titanium and silicon. The type and process parameters of the PVD method that enables the acquisition of DLC coatings are effective on the implant material corrosion resistance. Thus, it is concluded that DLC is suitable for use as a protective coating to protect against corrosion.

All these studies show that the effect of DLC coatings on medical materials used in the health field will be higher in the future. This review article was made to have information about the corrosion of DLC coatings. The importance of DLC coating in increasing corrosion resistance was emphasized. Developing economic products that are more compatible with the human body and which do not cause problems at the place of use of the implant and which can be used in a compatible and long-term manner will create promising developments on behalf of the health sector.

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