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# Wettability and Surface Free Energy of Ti(C,N) Coatings on Nickel-based Casting Prosthetic Alloys

K. Banaszek <sup>a</sup>, L. Klimek <sup>b,\*</sup><sup>a</sup> Medical University of Lodz, Department of General Dentistry, Chair of Restorative Dentistry, Pomorska 251, Łódź, Poland<sup>b</sup> Medical University of Lodz, Department of Dental Technology, Chair of Restorative Dentistry, Pomorska 251, Łódź, Poland

\*Corresponding author. E-mail address: leszek.klimek@umed.lodz.pl

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## Abstract

The production process of prosthetic restorations runs in two stages. In the first stage, the prosthetic foundation is produced of metal alloys. In the second stage, a facing material is applied on the produced element. In both stages, the wettability is significantly important, as well as the free surface energy relating to it. The quality of the obtained cast depends on the surface phenomena occurring between the metal alloy and the material of which the casting mould is made. The performed examinations also point to a relation between the ceramics joint and the base, depending on the wetting angle.

The aim of the presented paper was to examine influence of the composition of a Ti(C,N)-type coating on bases made of the Ni-Cr prosthetic alloy on the wettability and the surface free energy.

The test material were disks made of the Ni-Cr alloy with the diameter of 8 mm. The disks were divided into five groups, which were covered with Ti(C,N) coatings, with different amounts of C and N in the layer. In order to determine the surface free energy ( $\gamma_s$ ), the wetting angle was measured. Two measure liquids were applied: distilled water and diiodomethane.

The obtained results of the measurements of the water-wetting angles suggest that together with the increase of the ratio of nitrogen to carbon in the Ti(C,N) coating, the surface hydrophobicity increases as well. In all the samples, one can see a large difference between the energy values of the polar and the apolar components. The high values of the polar components and the low values of the apolar ones make it possible to conclude that these surfaces exhibit a greater affinity to the polar groups than to the apolar ones.

On the basis of the analysis of the surface free energy, one can state that covering the alloy with Ti(C,N)-type coatings should not decrease the adhesion of the ceramics to the alloy, whereas TiC coatings should lead to the latter's improvement. Due to their hydrophilicity, TiC coatings should decrease the adhesion of bacteria to the surface and hinder the formation of a bacterial biofilm.

**Keywords:** Dental alloys, Wettability, Contact angle, Surface tension, Surface free energy

## 1. Introduction

The laboratorial process of producing prosthetic restorations in the form of crowns and bridges runs in two stages. In the first

stage, the foundation is produced of precious and non-precious metals, as well as zirconium oxide. In the following stage, a facing material is applied on the produced structure, such as porcelain, acrylate or a composite. Both in the first and the second stage, the wettability and the related surface free energy are of

significant importance. The first production stage, in the case of metal alloys, is connected with a casting process. The quality of the obtained cast depends on the surface phenomena occurring between the metal alloy and the material of which the casting mould is made [1]. The flow of the liquid metal into the mould depends on the alloy force-in pressure, the surface tension and the viscosity of the alloy, as well as the wettability of the mould material [1]. In the second production stage, porcelain flows into and fills the irregularities of the surface, which favours a mechanical pinning of the facing layer in the metal surface after its complete burn-out. The filling degree of all the surface cavings is determined by such factors as the surface tension, the wettability and the ceramics viscosity.

The strength of the metal-ceramics joint has the key importance for the users of this type of prosthetic elements, as the most frequently observed damage is the facing ceramics popping off the metal base. This affects both the prosthesis's esthetics and durability. That is why a lot of focus is being made on applying surface treatments which would modify the surface in such a way so as to improve the quality of the joint. To the most frequently used treatments belong: abrasive blasting, etching of the base with different reagents, laser etching, the use of low-melting ceramics and firing in vacuum or argon atmosphere. Recently, due to the development of surface engineering, there have been attempts at applying various kinds of interlayers [2-9]. They are usually layers containing silicon, applied with sol-gel methods, or layers containing gold, the so-called 'Goldbonder™'. One should also note the Ti(C,N)-type layers characterizing in good mechanical and tribological properties, as well as – most importantly – biological ones [10]. The research performed so far has not exhibited any negative reactions of the human body cells [11]. What is more, the layers reduce the adhesion of bacteria to the metal surfaces covered with them, which is important for the orthodontic and prosthetic elements for which the maintenance of a proper hygiene is problematic [12, 13]. The preliminary examinations showed that they can also improve the adhesion of the ceramics to the metal bases [2, 3].

The performed tests point to a relation of the ceramics' joint and the base, depending on the wetting angle [14-16]. The wetting force exhibited by a given liquid is represented by its tendency for

spreading on the surface of a solid body [17]. The ability of the given liquid to spread on the surface can be described by means of measuring the angle between the liquid and the surface of the solid body. It is determined by a direct measurement of the angle between the tangent at the contact point of two phases and the base. If the liquid particles are attracted more strongly by the particles of the solid body, the liquid spreads more extensively on the surface. In the case of a weaker attraction, the wetting of the surface is low. The higher the tendency for surface wetting, the smaller the contact angle, up to the occurrence of complete wetting with the angle equaling zero [17]. It is assumed that, if, for water as the measure liquid,  $\Theta < 90^\circ$ , the surface is hydrophilic, and in the case of  $\Theta > 90^\circ$ , it is hydrophobic. In the case of ceramics firing on metal bases, the contact angle can be treated as a result of the balance between the surface and the energies of the applied ceramic materials. Its knowledge can help predict the behaviour of the liquid ceramics on the applied surfaces after different surface treatments and thus predict the quality of its joint with the base. This has an unquestionable importance for the further behaviour of these systems as well as their durability.

## 2. Research objective

The aim of the work was to examine influence of the composition of Ti(C,N)-type layers on its wettability by a polar and an apolar liquid as well as on the surface free energy.

## 3. Material and methods

The test material were disks made of the Ni-Cr alloy, 8 mm in diameter and 10 mm high (Figure 1). The initial composition of the alloy determined by the X-ray fluorescence analysis, with the use of the SRS300 spectrometer by SIEMENS, is given in Table 1.

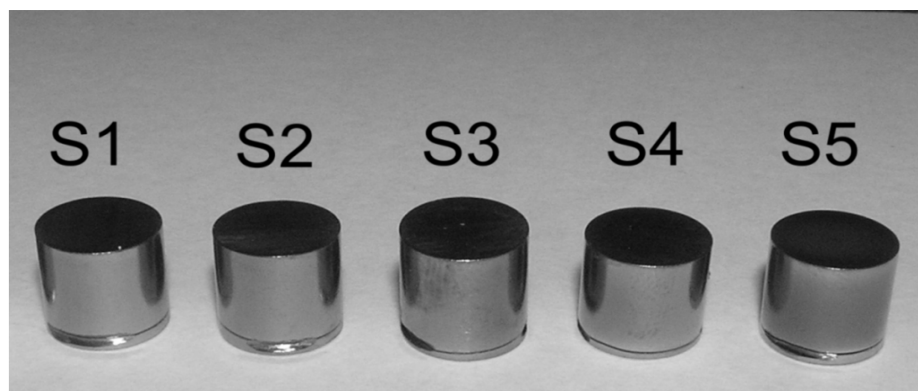


Fig. 1. Test samples

The disks were divided into five groups, which were coated with Ti(C,N) layers, with different amounts of C and N in the layer (Table 2). The coating was performed by the magnetron method [9].

Table 1.

Chemical composition of the examined alloy

Element content, % wt.						
Cr	Mo	Si	Fe	Co	Mn	Ni
24.79	8.89	1.57	1.33	0.17	0.12	residue

Table 2.

Chemical compositions of the examined layers

Layer	Element content, % wt.	
	C	N
S0	Sample without layer	
S1	100	0
S2	70	30
S3	63	37
S4	82	18
S5	0	100

In order to determine the surface free energy ( $\gamma_S$ ) of the tested samples, a measurement of the wetting angle was performed with the use of the apparatus by Krüss GmbH Germany, model FM40 EasyDrop. Two measure liquids were applied: distilled water and diiodomethane. The liquids were selected in such a way so that one of them had a low value of the dispersive component of surface energy ( $\gamma_L^d$ ), and a high value of the polar component of surface energy ( $\gamma_L^p$ ), whereas the other one – conversely – a high value of  $\gamma_L^d$ , and a low value of  $\gamma_L^p$ . The liquids were dosed in the amount of 0.8  $\mu$ l. The wetting angle was determined with the use of the DSA15 program, on the basis of the measurement of the geometry of a drop of the measure liquid placed on the examined surface. For the calculation of the value of the particular dispersive ( $\gamma_S^d$ ) and polar ( $\gamma_S^p$ ) components of the tested samples, the Owens-Wendt model was applied (equation 1). The components calculated in this way were used to determine the surface free energy of the examined layers (equation 2).

$$\gamma_L \frac{1+\cos\theta}{2} = (\gamma_S^d \gamma_L^d)^{0,5} + (\gamma_S^p \gamma_L^p)^{0,5} \quad (1)$$

$$\gamma_S = \gamma_S^p + \gamma_S^d \quad (2)$$

where:

$\theta$  - wetting angle [deg],

$\gamma_L$  - surface tension of the measure liquid [mJ/m<sup>2</sup>],

$\gamma_S$  - surface free energy of the examined material [mJ/m<sup>2</sup>],

$\gamma_L^p$  - polar component of the measure liquid [mJ/m<sup>2</sup>],

$\gamma_L^d$  - dispersive component of the measure liquid [mJ/m<sup>2</sup>],

$\gamma_S^p$  - polar component of the examined surface [mJ/m<sup>2</sup>],

$\gamma_S^d$  - dispersive component of the examined surface [mJ/m<sup>2</sup>].

On the basis of the literature data [18], the values of the particular components for water and diiodomethane were assumed, which are compiled in Table 3.

Table 3.

Polar and dispersive component values for the applied measure liquids

Liquid	$\gamma_L$ , mJ/m <sup>2</sup>	$\gamma_L^d$ , mJ/m <sup>2</sup>	$\gamma_L^p$ , mJ/m <sup>2</sup>
Distilled water	72.8	21.8	51
Diiodomethane	50.8	48.5	2.3

## 4. Test results

Exemplary images of a drop of the polar and apolar liquid on the surface of selected samples are shown in Fig. 2 – 7. The results of the measurements of the wetting angles for the tested liquids and the values of the surface free energy calculated on their basis are presented in Table 4.

Table 4.

Wetting angle and surface energy values of the examined samples

Sample	Wetting angle deg		Polar component	Apolar component	Energy mJ/m <sup>2</sup>
	Water	Diiodomethane			
S0	83	52.1	33.10	3.82985	36.92
S1	70.5	45.8	36.58	8.08916	44.67
S2	91.5	48	35.38	1.15480	36.54
S3	103.3	47.1	35.88	0.00007	35.88
S4	103.3	47.2	35.82	0.00013	35.82
S5	115.1	47.2	35.82	0.95674	36.78

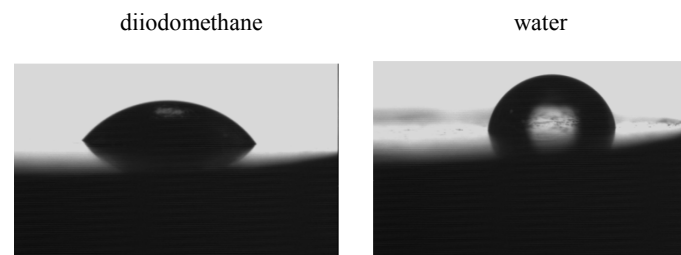


Fig. 2. Exemplary images of the drops of the used liquids on the surfaces of the samples S0

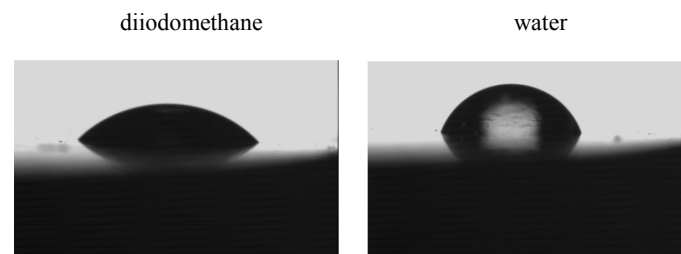


Fig. 3. Exemplary images of the drops of the used liquids on the surfaces of the samples S1

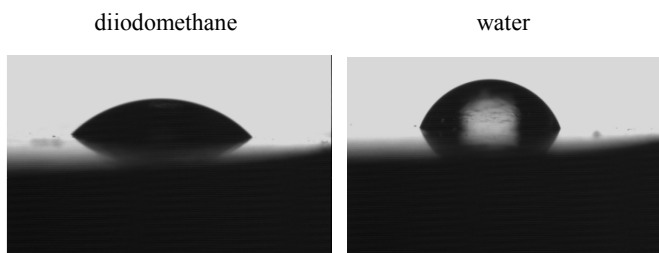


Fig. 4. Exemplary images of the drops of the used liquids on the surfaces of the samples S2

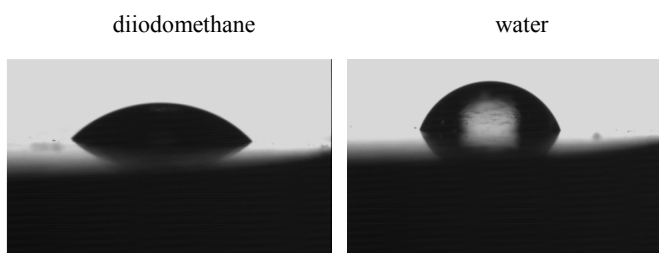


Fig. 5. Exemplary images of the drops of the used liquids on the surfaces of the samples S3

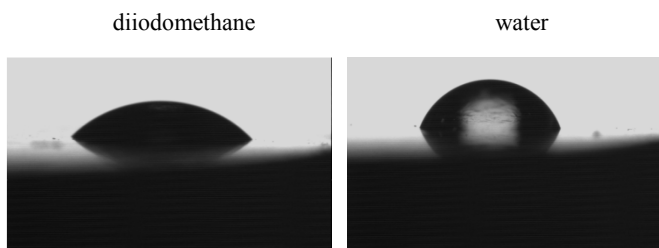


Fig. 6. Exemplary images of the drops of the used liquids on the surfaces of the samples S4

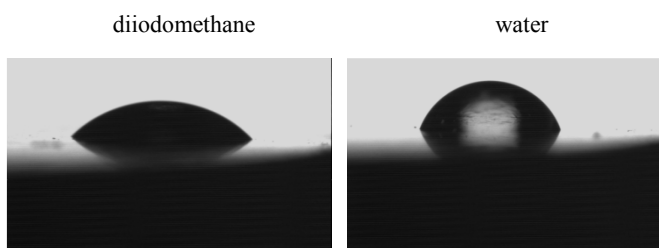


Fig. 7. Exemplary images of the drops of the used liquids on the surfaces of the samples S5

## 5. Discussion of results

The obtained measurement results for the water-wetting angles suggest that, together with the increase of the nitrogen-carbon ratio in the Ti(C,N) layers, the hydrophobicity of the surface increases as well, where: the surfaces of samples S3, S4 and S5 have a strong hydrophobic character, sample S2 lies at the border and samples S0 and S1 are hydrophilic. The strongest hydrophilic character is exhibited by sample S1.

In the analysis of the obtained results for the surface free energy, one can state that the highest values ( $44.67 \text{ mJ/m}^2$ ) were obtained for sample S1 (pure titanium carbide TiC). All the remaining samples, including the sample without coating, have similar values of the surface free energy (from  $37.89 \text{ mJ/m}^2$  for sample S4 to  $36.92 \text{ mJ/m}^2$  for the sample without coating).

In a closer analysis of the polar component values, we can see that all the coatings increase its values in relation to the alloy without coating. As regards the apolar component, sample S1 (TiC) has a higher value than the initial one, whereas, in the case of all the remaining ones, we can observe a significant decrease of this component value, in relation to the sample without coating. In all the samples, we can see a large difference between the values of the polar and the apolar component energies. The high values of the polar components and the low values of the apolar ones allow us to conclude that these surfaces have a stronger affinity to polar groups than to apolar ones.

The aspect of wettability, surface free energy, chemical composition and charge should be taken into consideration in the analysis of the factors favouring bacteria adhesion on the surface of prosthetic elements [19]. The physico-chemical properties of the surface, as well as its topography, hydrophobicity, charge and surface free energy have an effect on the bacterial cells [20, 21]. A high value of the free energy favours bacteria adhesion and biofilm formation [22]. It is thought that a hydrophobic character of the surface in a water environment favours the colonization of the majority of bacterial strains [23]. And so, by applying treatment which renders the surfaces hydrophilic, we reduce the bacteria's ability to colonize the prosthetic element and thus a further development and formation of a bacterial biofilm [24, 25].

Wettability also has a great importance for the retaining of the prosthesis in the oral cavity of the patient. The authors of works [26-28] suggest that an improvement of the prosthesis retention can be obtained by increasing the wettability of the surface.

## 6. Conclusion

To sum up, on the basis of the performed analysis of the wettability of the sample surfaces, we can state that layers S2, S3, S4 and S5 do not, in fact, change the surface free energy of the alloy, whereas the TiC layer (sample S1) increases it significantly. Coating the alloy with Ti(C,N)-type layers should not reduce the ceramics adhesion to the alloy, whereas coating it with a TiC layer should lead to its improvement as well as a reduction of the possibility of bacterial colonization of the prosthetic elements covered with this coating.

## References

- [1] Pucka, G., Orlicki, R. & Rączka, K. (1986). Wettability of Mikromed 1-04, Wironit, Magnum and Remanium dental alloys. *Prot. Stom.* 36(1), 10-13 (in Polish).
- [2] Park, S.W., Kim, J.M., Lim, H.P., Oh, G.J., Kim, H.S., Ong, J.L. & Lee, K.M. (2009). Gold and titanium nitride coatings on cast and machined commercially pure titanium to improve titanium-porcelain adhesion. *Surf. Coat. Tech.* 203, 3243-3249. DOI: 10.1016/j.surfcoat.2009.04.004.
- [3] Lim, H.P., Kim, J.M., Lee, K.M. & Park, S.W. (2011). Fracture load of titanium crowns coated with gold or titanium nitride and bonded to low-fusing porcelain. *J. Prosthet. Dent.* 105, 164-170. DOI:10.1016/S0022-3913(11)60023-1.
- [4] Elsaka, S.E., Hamouda, I.M., Elewady, Y.A., Abouelatta, O.B. & Swain, M.V. (2010). Effect of chromium interlayer on the shear bond strength between porcelain and pure titanium. *Dent. Mater.* 26(8), 793-798. DOI: 10.1016/j.dental.2010.04.004.
- [5] Homann, F., Waddell, J.N. & Swain, M.V. (2006). Influence of water, loading rate and bonder on the adhesion of porcelain to titanium. *J. Dent.* 34, 485-490.
- [6] Suansuwan, N. & Swain, M.V. (2003). Adhesion of porcelain to titanium and titanium alloy. *J. Dent.* 31, 509-518.
- [7] Yamada, K., Suansuwan, N., Sumii, T. & Swain, M.V. (2001). Comparison of the bonding strength of porcelain with different bonding systems and alloys as measured by interfacial toughness. *J. Dent. Research.* 80, 754.
- [8] Yamada, K., Onizuka, T., Endo, K., Ohno, H. & Swain, M.V. (2005). The influence of Goldbonder and pre-heat treatment on the adhesion of titanium alloy and porcelain. *J. Oral Rehabil.* 32(3), 213-220.
- [9] Zhang, H., Guo, T.W., Song, Z.X., Wang, X.J. & Xu, K.W. (2007). The effect of ZrSiN diffusion barrier on the bonding strength of titanium porcelain. *Surf. Coat. Tech.* 201(9-11), 5637-5640.
- [10] Banaszek, K., Pietnicki, K. & Klimek, L. Effect of carbon and nitrogen content in Ti(C,N) coatings on selected mechanical properties. *Metal Forming* (in press).
- [11] Sokołowski, J. (2001). *Usefulness evaluation of titanium nitride protective coatings on metal elements of prosthetic restorations*. Habilitation thesis. Medical University of Lodz, Lodz, Poland (in Polish).
- [12] Klimek, L. (2006). Adhesion of bacteria on modified surfaces of prosthodontic Co-Cr-Mo alloy. Initial examinations. *Surface Engineering.* 4, 64-68 (in Polish).
- [13] Klimek, L., Jakubowski, W. & Banaszek, K. (2007). Bacteria adhesion to modified surfaces of prosthodontic Ni-Cr-Mo alloy. A preliminary study. *Dental Prosthetics.* 1(LVII), 60-64 (in Polish).
- [14] Sharifa Al-Shehri, A., Hamdi, M.A. & Wilson, C.A. (1996). Influence of lamination on the flexural strength of a dental castable glass ceramic. *J. Prosthet. Dent.* 1, 23-28. DOI: 10.1016/S0022-3913(96)90341-8.
- [15] Mc Lean, J.V. (1991). The science and art of dental ceramics. *Oper. Dent.* 16, 149-156.
- [16] Oilo, G. (1988). Flexural strength and internal defects of some dental porcelains. *Acta. Odontol. Scand.* 46, 313-322.
- [17] Craig, R.G. (2006). *Dental materials*. Wrocław: Elsevier Urban & Partner (in Polish).
- [18] Dann, J.R. (1970). Forces involved in the adhesive process. I Critical surface tensions of polymeric solids as determined with polar liquids. *J. Coll. Interf. Sci.* 32, 302-320.
- [19] Pieczyńska, D., Ostaszewska, U., Bieliński, D.M. & Jagielski, J. (2011). Modification of polymers with the application of ion beam bombardment. Part I. History, recent developments, and perspectives for development. *Polymers.* 56(6), 439-451. (in Polish).
- [20] Katsikogianni, M. & Missirlis, Y.F. (2004). Concise review of mechanisms of bacterial adhesion to biomaterials and of techniques used in estimating bacteria-material interactions. *Eur. Cell Mater.* 8, 37-57.
- [21] Park, B.S., Heo, S.J., Kim, C.S., Oh, J.E., Kim, J.M., Lee, G., Park, W.H., Chung, C.P. & Min, B.M. (2005). Effects of adhesion molecules on the behavior of osteoblast-like cells and normal human fibroblasts on different titanium surfaces. *J. Biomed. Mater. Res. A.* 74, 640-651.
- [22] Sobolewska, E., Frączak, B., Błażewicz, S., Seńko, K. & Lipski, M. (2009). Comparison of wetting contact angle of basic prosthetic materials used in the fabrication of removable dentures in an in vitro study. *Dental Prosthetics.* 6(LIX), 401-406 (in Polish).
- [23] Gristina, A.G. (1987). Biomaterial-centered infection: microbial adhesion versus tissue integration. *Science.* 237, 1588-1595.
- [24] Kazemzadeh-Narbat, M., Lai, B.F., Ding, C., Kizhakkedathu, J.N., Hancock, R.E. & Wang, R. (2013). Multilayered coating on titanium for controlled release of antimicrobial peptides for the prevention of implant-associated infections. *Biomaterials.* 34, 5969-5977. DOI: 10.1016/j.biomaterials.2013.04.036.
- [25] Ochsner, P.E., Majewski, M. & Plaass, C. (2006). Infection after osteosynthesis: a summary of the scientific presentations at the annual Swiss AO meeting 2005 in Liestal. In Annual Swiss AO meeting, 2005L 117-119. Injury: Elsevier Sci Ltd.
- [26] O'Brien, W.J. & Ryge, G. (1965). Wettability of poly(methyl-methacrylate) treated with silicone tetrachlorid. *J. Prosthet. Dent.* 15, 304-308.
- [27] Boucher, L.J., Ellinger, C., Lutes, M. & Hickey, J.C. (1968). The effect of a microlayer of silica on the retention

of mandibular complete dentures. *J. Prosthet. Dent.* 19, 581-586.

[28] Gesser, H.D. & Castaldi, C.R. (1971). The preparation and evaluation of wetting dentures for adhesion and retention. *J. Prosthet. Dent.* 25, 235-243.