Effects of shot-peening on surface contact angles of biomaterials

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It was shown previously that (i) if the surface of a biomaterial is covered with TiO_2 (tetragonal structure oxide), it shows a high initial contact angle and a high change rate in contact angle (i.e. a higher spreading process); while (ii) cubic structure oxides show relatively lower spreading rates in 1% NaCl solution at 25 °C. Shot-peening has been applied to biomaterials (especially titanium and its alloys) to improve their fatigue strength. It is well known that shot-peening causes surface roughening. The effects of surface roughness on wettability are not well documented. Therefore, in the present study, the effects of shot peening on the initial contact angle and changes in it as a function of time, were investigated. In addition, the spontaneous half-cell potential of all tested biomaterials were measured to correlate the wettability phenomenon to initial surface chemistry. Pure titanium and its alloys, including Ti–6Al–4V and NiTi alloys, AISI Type 316L stainless, Co–Cr alloy, and pure nickel, were mechanically polished, shot-peened and pre-oxidized at 300 °C for 30 min in pure oxygen. It was found that (i) shot-peening homogenized the surface conditions in terms of initial contact angles, (ii) TiO_2 oxide shows a higher spreading coefficient, while cubic structure oxides show a lower value, and (iii) the spreading coefficient was correlated to the magnitude of the spontaneous half-cell potential.

1. Introduction

In a previous study [1], it was found that the wettability and the spreading phenomena of biomaterials in a drop of 1% NaCl solution can be related to the crystalline structures of the surface oxide film. Namely, TiO_2 (rutile: tetragonal structure) – except for oxides formed on Ti–6Al–4V – showed a high initial contact angle, θ_0, with a high change rate, $\delta\theta/\delta t$; while a slow spreading coefficient, $\delta\theta/\delta t$, was observed on cubic structure oxides (i.e. NiO formed on pure nickel and spinel types formed on both 316L stainless steel and Co–Cr alloy).

It is well documented that shot-peening has been employed as an effective way to improve characteristics, especially in terms of improved fatigue behaviour and/or corrosion resistance of metallic materials [2]. This improvement is recognized as enhanced fatigue strength or reduced fatigue crack growth, and also retardation in the susceptibility to stress corrosion cracking [3, 4]. Because only the surface layer is plastically deformed by shot-peening and the bulk material remains undeformed, this inhomogeneous deformation induces compressive residual macrostresses in a relatively thin surface layer [2]. Because residual stresses act as if they are mean stresses in the fatigue cycling process, compressive residual stress developed at the surface layers reduces the mean stress in the surface layer, resulting in the retardation of the initiation of early fatigue crack growth [2, 5].

Research in the biomedical applications of shot-peening has been limited. For instance, Eylon and Froes [6] reported that the fatigue strength of powder-metallurgy manufactured titanium, which has 1% – 2% porosity, can be improved by the shot-peening which causes a closure of outer pores as well as simultaneously strain-hardening the surface.

A fracture-resistant implant alloy for highly stressed anchorage stems for femoral prostheses should have a minimum rotating bending fatigue strength of 400 N mm^{-2}. It has been reported that this minimum requirement is met not only by cold-worked Co–Ni–Cr–Mo, hot-forged Co–Ni–Cr–Mo, and

Co–Cr–Mo alloys with variable deformation rates and a shot-peened surface, but also by hot-forged and shot-peened Ti–Al–V alloy [7].

Moreover, Dobbs and Robertson [8], studying the fatigue strength and the corrosion behaviour of Ti–6Al–4V and Ti–4Mo–4Al–2Sn alloy in Ringer's solution, concluded acid-etching and shot-peening treatment resulted in a slight anodic shift and a 100% increase in the passive current density. Also, it was reported that for Ti–6Al–4V alloy, the passive current density was decreased by anodization, but was increased by passivation and steam sterilization and by acid-etching treatment, followed by shot-peening [8].

Various studies have used the surface contact angle as a measure to characterize the surface layer of biomaterials [9, 10]. It should be mentioned here that shot-peening treatment causes an increase surface roughness. The effect of surface roughness on the contact angle measurements has not been well documented. It has been reported that the roughness of a surface has the effect of making the contact angle greater than 90°; if smooth material shows an angle greater than 90°, roughness increases this angle even further. For example, on rough paraffin wax, the contact angle is 132°, compared with about 110° on smooth wax [11]. However, if θ is less than 90°, roughness decreases the contact angle [11]. When a solid surface exhibits a roughness, there is evidence that the adhesion capability in terms of $W(= S (1 + \cos\theta))$ is increased above the value for smooth surfaces [12], because θ decreases, resulting in increasing $\cos\theta$, where W is the unit work of adhesion and S is the surface tension of a liquid. It is also recognized that high degrees of correlation between contact angle measurements and various biological interactions exist [9, 10, 13–16].

The purpose of this study was to examine the effects of shot-peening on the surface contact angles and their changes as a function of time (i.e. a time-dependent spreading coefficient) on various biomaterials.

2. Test materials and experimental procedures

The test specimens consisted of various biomaterials, which included pure titanium, Ti–6Al–4V alloy, Ti–50 at% Ni (martensitic phase having $M_s \sim 50\,°C$), Ti–51 at% Ni (austenitic phase having $M_s \simeq 0\,°C$), AISI Type 316L stainless steel, Co–Cr alloy, and pure nickel.

Surfaces of all the tested biomaterial coupons (25 mm × 25 mm × 2 mm), after mechanical polishing (with metallographic paper, grit no. 600), were shot-peened by using glass beads (shot size GP 60–100) at an intensity of 4–6 Almen A providing 100% coverage (performed by the Metal Improvement Company). Surface coverage by shot-peening was examined by using the PEENSCAN technique developed by the Metal Improvement Company [17]. The shot-peened surfaces were then pre-oxidized at 300 °C for 30 min in pure oxygen.

A sessile drop of 1% NaCl solution was used for the surface contact angle measurements. Three readings

were made and the average value had a standard deviation of ± 3.0° to ± 5.0° in θ. For further understanding of the surface phenomena, the spontaneous half-cell potential of the pre-oxidized shot-peened surfaces was measured in 1% NaCl solution against a saturated calomel electrode (SCE) at 25 °C.

3. Results and discussion
3.1. Mircostructures of shot-peened surfaces
Figs 1 and 2 show surface and cross-sectional microstructures (unetched conditions) of both mechanically polished and shot-peened conditions of Ti–6Al–4V alloy. As shown in Fig. 2, the shot-peened surface shows a plurality of indentations marked by round-shaped shot beads. The average size of the shot indentation is approximately 40–50 μm, which is the same as the surface roughness of about 40–50 μm (see bottom photograph, Fig. 2).

3.2. Contact angles of shot-peened biomaterials
Fig. 3 shows the initial contact angle, θ_0, measured by using 1% NaCl aqueous solution at room temperature. In a previous study [1], an alpha-alumina plate was also tested; however, because the surface hardness of alpha-alumina is much higher than that of the glass beads used for shot-peening, in this study, it was speculated that shot-peening may not have any effect on this material. Therefore, this material was excluded in the present study.

The average value of the initial contact angle was 55.05° ± 6.8°, while it was 55.39° ± 14.6° for the mechanically polished conditions [1]. Referring to Fig. 4, there is a 50–50 possibility for the advancing
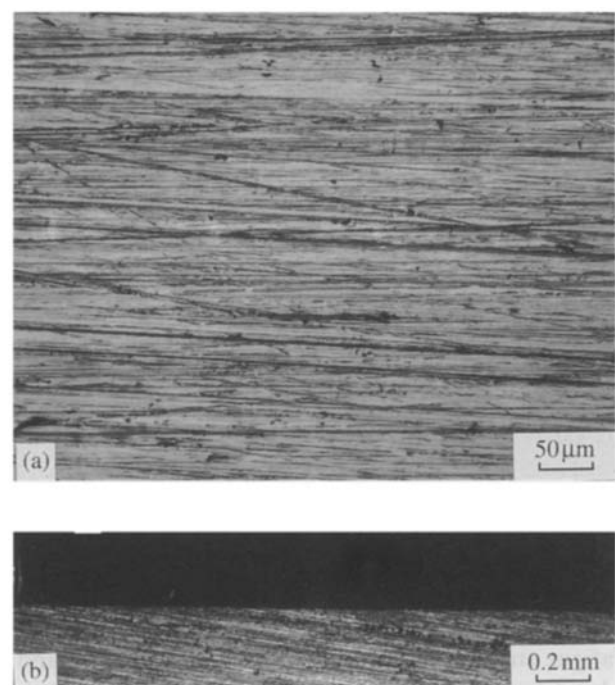

Figure 1 Surface and cross-sectional microstructures of mechanically polished Ti–6Al–4V. (a) surface, (b) cross-section.
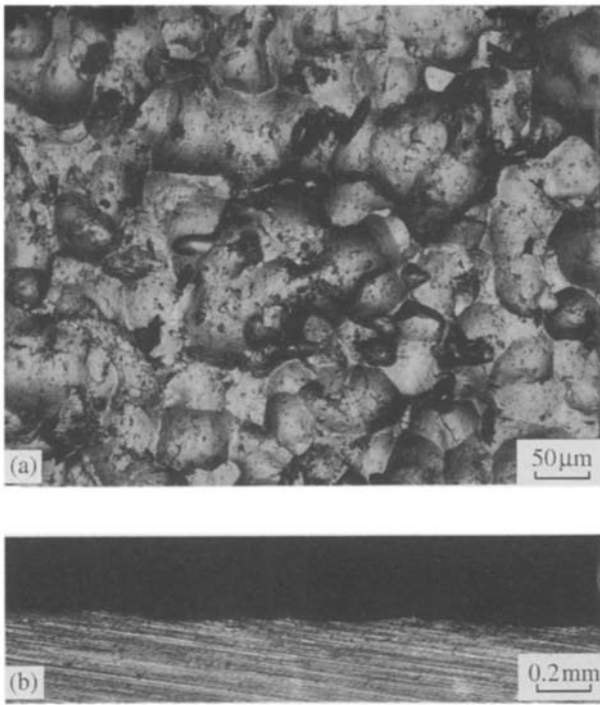
Figure 2 Surface and cross-sectional microstructures of shot-peened Ti–6Al–4V. (a) surface, (b) cross-section.

front to approach the up-hill portion and down-hill portion of the shot indentation, which is about 40–50 μm apart as well as in height. If the advancing front sits on the down-hill portion, the localized contact angle will be lower than the circumstance where it sits on the up-hill portion. The number of these local-

ized uneven sites will be approximately from 600 sites ($2\pi r/50$ μm, where r is the radius of a single drop, being about 10 mm in this study) to 750 sites ($2\pi r/40$ μm). The measured contact angle, therefore, will be averaged over these uneven sites. On the other hand, although the mechanically polished surfaces appear to be flatter macroscopically than the shot-peened surfaces, the surface roughness depends upon the surface hardness. Therefore, it may be said that the initial contact angle is principally controlled by the surface geometry. A smaller standard deviation found in the shot-peened surfaces than the mechanically polished surfaces might also be due to the fact that the thickness of the oxide film depends on the degree of plastic deformation on the substrate surface layers [18]. Although the roughness on the shot-peened surface is higher than that on the mechanically polished surface, after the oxide film was formed on these surfaces, the locally irregular geometry might be minimized, on particular shot-peened surfaces. Hence, shot-peening homogenized the initial contact angles.

Fig. 5 shows changes in contact angles as a function of time. If h is the height and d is the length of a sessile drop, the contact angle, θ, can be related to $\theta = 2$ arctan $(2h/d)$. Because both h and d change with time, the time-dependent θ variation can be expressed as $\delta\theta/\delta t = [-4h(\delta d/\delta t) + 4d(\delta h/\delta t)]/(d^2 + 4h^2)$ in rad./time unit. Table I shows a comparison between the initial contact angles, θ_0, and their changes, $\delta\theta/\delta t$, measured on the shot-peened surfaces with those obtained for the mechanically polished surfaces (reported in a previous study [1]). All data points listed in
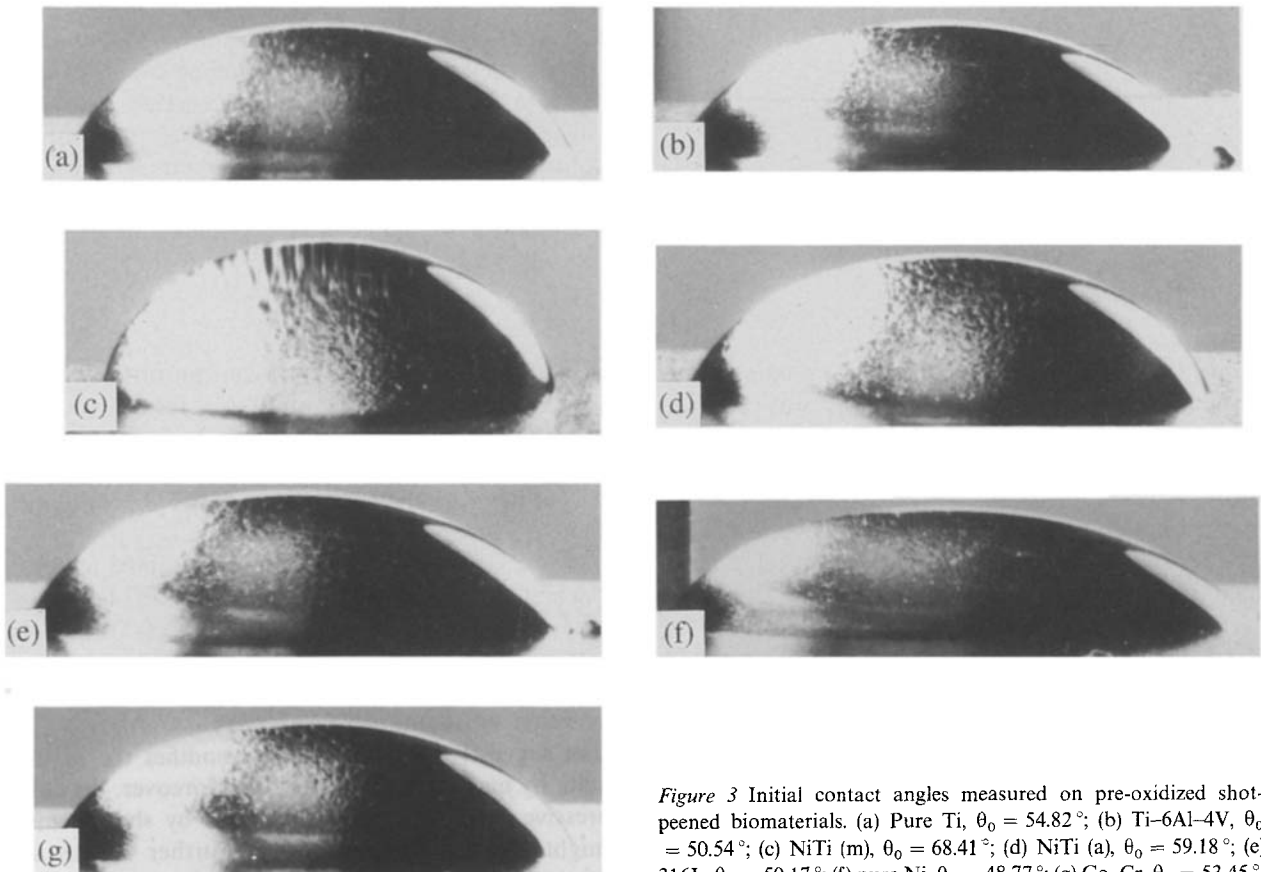

Figure 3 Initial contact angles measured on pre-oxidized shot-peened biomaterials. (a) Pure Ti, $\theta_0 = 54.82°$; (b) Ti–6Al–4V, $\theta_0 = 50.54°$; (c) NiTi (m), $\theta_0 = 68.41°$; (d) NiTi (a), $\theta_0 = 59.18°$; (e) 316L, $\theta_0 = 50.17°$; (f) pure Ni, $\theta_0 = 48.77°$; (g) Co–Cr, $\theta_0 = 53.45°$.

Up-hill
Down-hill

Time

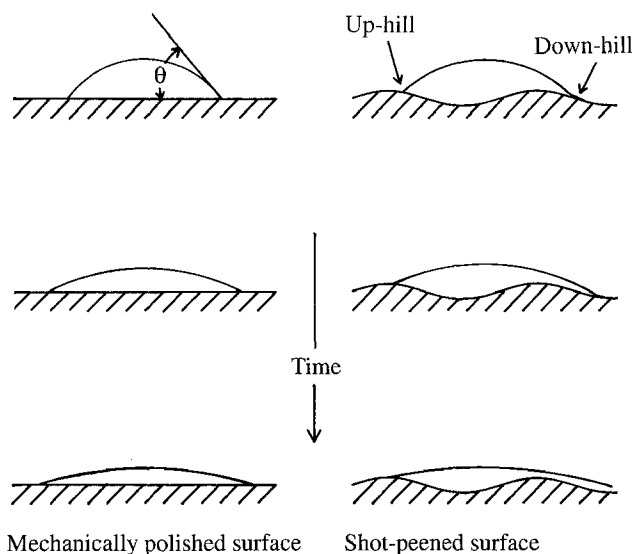Mechanically polished surface   Shot-peened surface

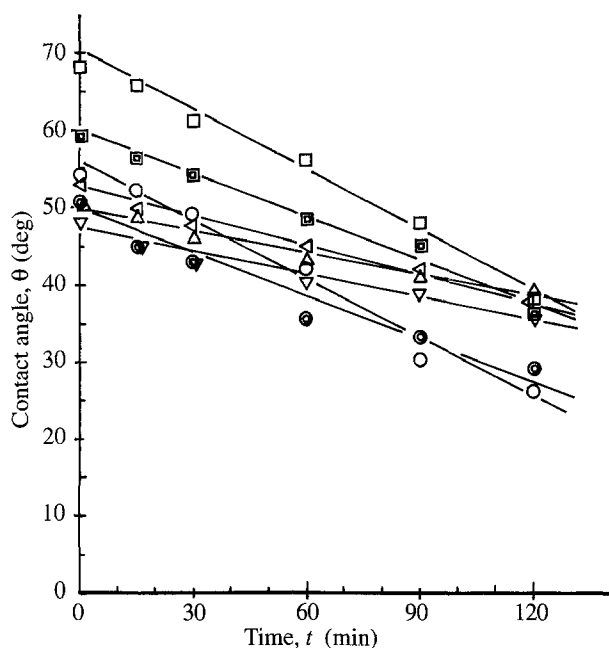*Figure 4* Surface geometry effect on contact angles.

Figure 5 Contact angles versus time. Mechanical polishing $\longrightarrow$ shot-peening $\longrightarrow$ oxidizing (30 °C, 30 min in O_2) 1% NaCl solution. ($\bigcirc$) Pure Ti, ($\bigcirc$) Ti–6Al–4V alloy, ($\square$) NiTi (m), ($\square$) NiTi (a), ($\triangle$) 316L, (∇) pure Ni, ($\triangleleft$) Co–Cr.

TABLE I Initial contact angles and changes in contact angles as a function of time

	m.p. $\rightarrow$ oxidizing		m.p. $\rightarrow$ s.p. $\rightarrow$ oxidizing	
	θ_0 (deg)	$\delta\theta/\delta t$	θ_0 (deg)	$\delta\theta/\delta t$
Pure Ti	54.24	− 0.0046	54.82	− 0.0045
Ti–6Al–4V	32.08	− 0.0010	50.54	− 0.0034
NiTi (m)	69.88	− 0.0055	68.41	− 0.0046
NiTi (a)	71.79	− 0.0048	59.18	− 0.0033
316L s.s.	56.46	− 0.0024	50.17	− 0.0013
Pure Ni	35.72	− 0.0016	48.77	− 0.0016
Co–Cr alloy	62.04	− 0.0023	53.45	− 0.0018
Alpha alumina	60.87	− 0.0044	–	–

was formed on Ti–6Al–4V alloy. Also, both TiNi alloys were covered with a mixture of TiO_2 and $NiTiO_3$. Furthermore, NiO was formed on pure nickel. Both 316L stainless steel and Co–Cr alloy were covered with a spinel-type oxide, such as $M'O \cdot M''_2O_3$, where M' represents Fe^{2+} and/or Ni^{2+}, or Co^{2+}, and M'' represents Fe^{3+} and/or Cr^{3+}.

It is of interest to note that materials in group 1 (see Table I) are covered with oxide films which are cubic structures that include face-centred cubic for the spinel-type oxides formed on 316L stainless steel and Co–Cr alloy, and simple cubic structure of NiO formed on pure nickel. On the other hand, group 2 materials have surfaces covered with tetragonal TiO_2. The degree of change in the contact angle as a function of time on these two oxides is different, as described above. Although it is not clear, at this moment, how to explain this phenomena, the differences in the surface polarity might be attributable to this phenomenon. It is known that TiO_2 is a metal-excess semiconductor (n-) type oxide, while NiO and spinel-type oxides are metal-deficit semiconductors (p-) type oxides [19].

From the contact angle measurements, it may be suggested that (i) the initial contact angle, θ_0, is mostly controlled by the surface geometry, and (ii) the change in contact angle, $\delta\theta/\delta t$, is dependent upon the type of crystalline structure of the oxide films formed on the surface of a biomaterial.

Table I are averaged values for three readings. The standard deviation of the measures was between $\pm 3.0°$ and $\pm 5.0°$ for θ (in degrees).

This study showed that changes of contact angles, $\delta\theta/\delta t$, of shot-peened surfaces may be classified into two groups; (1) low $\delta\theta/\delta t$ (negative value) for 316L stainless steel, Co–Cr alloy and pure nickel, and (2) high $\delta\theta/\delta t$ for pure titanium, Ti–6Al–4V alloy, and NiTi alloys.

Nakayama and Oshida [18], studying crystalline structures of oxide films formed on shot-peened surfaces in high-temperature water (at 300 °C), reported that oxide films formed on shot-peened surfaces were identical to those formed on mechanically polished surfaces of AISI Type 304 and 316 stainless steels. Our previous studies demonstrated that TiO_2 was formed on pure titanium, and a mixture of TiO_2 and Al_2TiO_5

3.3. Half-cell potential measurements
Pre-oxidised shot-peened surfaces of the test coupons were coupled to a saturated calomel electrode (SCE) through a d.c. voltometer to measure the spontaneous half-cell potentials in 25 °C 1% NaCl aqueous solution.

Table II summarizes the results obtained for both the half-cell potentials of oxidized surfaces of mechanically polished and shot-peened surfaces. It was observed that shot-peening produced surface conditions with a more noble state than that of the mechanically polished surfaces (except Co–Cr alloy). This observation suggests that shot-peening modifies the surface state by making it more passive. Moreover, the compressive residual stresses developed by shot-peening might affect surface chemistry. Further studies are needed to gain full understanding of this phenomenon.

TABLE II Half-cell potential of biomaterials

	E(V) versus SCE at 25 °C	
	m.p. →oxid.	m.p. →s.p. →oxid.
Pure Ti	0.145	0.165
Ti–6Al–4V	0.087	0.156
NiTi (m)	0.075	0.145
NiTi (a)	0.091	0.135
316L	0.037	0.085
Pure Ni	0.056	0.101
Co–Cr	0.108	0.107

In 1% NaCl solution

It was also found, among various shot-peened surfaces, that TiO_2 (tetragonal structure oxide) shows a more noble surface state than the cubic structure oxides (i.e. spinel-type oxides and simple cubic NiO). The pH value of 1% NaCl solution measured at 25 °C was 7.3. According to the Pourbaix's diagram (pH and potential diagram) [20], all surfaces of the tested biomaterials can be found in the passive regime. Although the initial contact angles of pre-oxidized shot-peened biomaterials showed similarity (i.e. approximately 50°–60° in θ, see Table I), the time-dependent spreading coefficient, δθ/δt, seems to be dependent upon type of oxide films.

During the insertion and operation of implantable biomaterial, if the surface passive film is broken mechanically, it is believed that all tested materials (except pure nickel) possess the capability for rapid repassivation. This provides for excellent corrosion resistance for these materials. However, this re-healing process of the broken passive films depends on the repassivation potential of the material in a certain electrolyte (mostly body fluids). Therefore, if the half-cell potential is higher (in other words, more noble), the repassivation capability is better. Furthermore, because of a higher spreading coefficient of the TiO_2 film, one may expect better blood- or fluid-wettability in titanium-based alloys.

4. Conclusions

Surface layers of pure titanium and its alloys (Ti–6Al–4V and NiTi alloys), 316L stainless steel, Co–Cr alloy, and pure nickel, were shot-peened and pre-oxidized at 300 °C for 30 min. The effects of shot-peening on contact angles were investigated using a sessile drop of 1% NaCl aqueous solution at room temperature. The spontaneous half-cell potential was also measured against a saturated calomel electrode (SCE) in 1% NaCl solution at 25 °C. Based upon this study the following conclusions may be drawn.

1. The initial contact angle, θ_0, is controlled by the surface geometry. Shot-peened surfaces exhibit smaller initial contact angles and standard deviation than mechanically polished surfaces as a result of homogenization of the surfaces.

2. Changes in contact angle as a function of time, (δθ/δt: a time-dependent spreading coefficient), are strongly dependent upon the type of surface oxide; a higher spreading rate is observed on biomaterials whose surfaces are covered with TiO_2; while a lower spreading coefficient is seen on cubic structure oxides including spinel-type oxides formed on stainless steel and Co–Cr alloy, and NiO oxide formed on pure nickel.

3. The spontaneous half-cell potential versus SCE indicated that all surfaces are in the passive regime. Shot-peening gave to the surface conditions a more noble state. It was also found that TiO_2 film showed a more noble state than the cubic structure oxides, suggesting that TiO_2 has a higher capability for re-passivation.

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