Effect of Sandblasting on the Oxidation and Corrosion Behaviour of an Oxide-Dispersed Strengthened (ODS) FeCrAl Alloy

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(Received on July 17, 2000; accepted in final form on September 19, 2000)

Metallic biomaterials are preferred for replacements of the hard tissues since they are the most suitable to withstand the mechanical loads. For some components the higher surface roughness is preferred to increase the adherence and anchorage between the implant and the bone. In this work sandblasting prior to the oxidation is used to increase the surface roughness of the oxide dispersion strengthened (ODS) FeCrAl alloy. The effect of sandblasting on its oxidation and corrosion behaviour is studied. As a comparison, polished samples are also studied. The alloy treated at 1 100°C generates a dense α-alumina layer which thickness increases with increasing exposure time, being the values somewhat lower for the sandblasted samples. Impedance diagrams obtained for sandblasted samples preoxidised for 1 and 3 h show impedance values at the lowest frequency two orders of magnitude lower than those for polished samples. This decrease in the impendence value can be attributed to the presence of paths or fine cracks in the alumina layer that communicate the aggressive medium with the metallic substrate. Spallation of the alumina layer in preoxidised sandblasted samples has been detected by electrochemical impedance spectroscopy for treatment times of 10 and 100 h. Despite this loss of the scale integrity, the corrosion behaviour is good.

KEY WORDS: oxidation; corrosion; electrochemical impedance spectroscopy (EIS); sandblasting; roughness.

1. Introduction

Metallic biomaterials are preferred for replacements of the hard tissues of the human body since they are the most suitable to withstand the mechanical loads they have to bear. Despite their good biocompatibility and biofunctional- ity, some problems have been reported after relatively long-term periods of service. One of the most important setback is the production of wear debris at the articulating surfaces and their accumulation in the adjacent tissues. The significance of ion release is also a topic of interest, since once ions are incorporated into the organic fluids they could be accumulated even at organs distant from the implant. To suppress or minimise these problems, various metallic alloys able to form a ceramic coating by thermal oxidation treatments have been proposed as potential biomaterials. In the case of the ODS ferritic alloys preoxidation treatment gives rise to the formation on the surface of a fine, but dense and tightly adherent α-alumina layer. Such adherence may be lost, however, if for instance the surface roughness of the substrate is substantially increased.

On the other hand, the interaction between cells and implants is governed by the physicochemical properties of the material’s surface, among which a major factor is the surface topology. As a matter of fact, the different components of a prosthesis may exhibit different surface finishing. For instance, components replacing the cup/ball have a mirror-like finish, whereas the stems inserted in the bone have a higher surface roughness to increase the adherence between the implant and the bone compared to those with a smooth surface. Within the surface engineering techniques, sandblasting is widely used to improve the mechanical performance of various types of components.

The aim of this work is to create on a ODS FeCrAl alloy a topologically modified surface by sandblasting and to study its effect on the oxidation and corrosion behaviour. The significance on the corrosion behaviour is studied by electrochemical impedance techniques and anodic polarisation tests. The influence of scale thickness is assessed by using different exposure times during oxidation. For comparative purposes, samples without oxidation treatment have also been studied.

2. Materials and Methods

The alloy studied is a commercial iron base superalloy produced by a powder metallurgy route consisting of mechanical alloying and thermomechanical treatments. The chemical composition (wt %) is: 20Cr, 5Al, 0.5Ti, 0.5Y₂O₃, 0.01C, balance Fe.

The material was supplied by Inco Alloys Limited, Hereford (UK) as hot rolled bars of 9.5 mm diameter. Rods of 9 mm diameter and 35 mm long were mechanically removed from the bar. Prior to the oxidation a set of samples
were polished and others sandblasted. The former were abraded on successive finer silicon carbide papers, then mechanically polished with 1 μm alumina paste to achieve a mirror-like finish. Sandblasting was obtained by shooting with corindon particles for 30 min. Prior to the oxidation, all samples were properly cleaned. Sandblasted samples were brushed and then cleaned in a jet of pressurised air to eliminate the residual particles adhered to the surface. Finally, all samples were washed in running water, and then ultrasonically cleaned for 20 min in alcohol.

The surface roughness of non-oxidised samples was measured using a profile meter Mitutoyo Surf Test 401. The measurements were obtained from line profiles perpendicular to the groove direction. The surface roughness was characterised by $R_a$, in μm.

Preoxidation of the samples was performed at 1100°C for different treatment times: 1, 3, 10 and 100 h, which led to scales of different thickness.

Microstructure studies were performed by scanning electron microscopy (SEM), energy dispersive X-ray (EDX) analysis, and wavelength dispersion X-ray microanalysis (WDX). To prevent the scale loss during the metallographic preparation, preoxidised samples were coated with a thin sputtered gold layer and then with a thicker layer of copper which was electrolytically deposited. Cross-sections were prepared by conventional metallographic techniques. The final surface polish was performed using diamond paste of 1 μm. The microstructure was revealed with an etchant consisting of 80% ethanol, 15% HCl, and 5% HNO₃.

The corrosion tests were performed in a three-electrodes cell used in electrochemical tests. Saturated calomel and platinum wire electrodes were used as reference and auxiliary electrodes, respectively, and as working electrodes the sandblasted samples in as-received and preoxidised conditions were used. The electrochemical tests were conducted in aerated Hank's solution at pH 7.4 and room temperature, which simulates the aggressive physiological fluids of the human body. The chemical composition of the electrolytic medium is given in Table 1.

![Figure 1](image)

Table 1. Chemical composition (g/l) of the Hank's solution.

| NaCl | CaCl₂ | KCl | NaHCO₃ | Glucose | MgCl₂.6H₂O | Na₂HPO₄.2H₂O | KH₂PO₄ | MgSO₄.7H₂O |
|------|-------|-----|--------|---------|-------------|--------------|---------|-------------|
| 8    | 0.14  | 0.4 | 0.35   | 1       | 0.1         | 0.06         | 0.06    | 0.06        |

The corrosion behaviour was studied by using electrochemical techniques, such as electrochemical impedance spectroscopy (EIS) and anodic polarisation tests. EIS was performed by applying a sinusoidal wave of 10 mV in amplitude to the working electrode at a frequency range from 64 kHz to 1 mHz. Anodic polarisation curves were drawn from the corrosion potential to the breakdown potential. At this potential a cathodic sense was imposed until the new corrosion potential was achieved. The curves were registered at a scanning rate of 0.6 V/h.

3. Results

Figure 1 shows the surface micrographs of the sandblasted and polished samples. The sandblasted samples show an irregular surface containing sharply converging protrusions resulting from the severe plastic deformation (Fig. 1a). SEM examination and EDX analysis showed a scarce contamination with corindon particles. The polished samples show grooves which are perpendicular to the longitudinal direction of the sample (Fig. 1b). The roughness of the sandblasted and polished samples was determined as less than 4 μm and 0.2 μm, respectively. The microstructure of the alloy in the as-received condition consists of very small grains slightly elongated in the longitudinal bar direction, about 4–5 μm in length and 0.5 μm in width.

Thermal oxidation of the samples at 1100°C gives rise to the formation of a nearly pure α-alumina scale. At the outer surface, small Ti-, Y-, or Fe-rich oxide nodules were observed. Cross-sectional examination reveals the formation of a scale tightly adherent to the substrate, but uneven in the case of sandblasted samples, (Fig. 2). The average thickness of the scale increases with increasing exposure time, being the thickness values somewhat lower for the sandblasted samples, as can be seen in Fig. 3.

On the other hand, the heat treatment causes grain growth of the substrate giving rise to the formation of large grains strongly elongated in the longitudinal bar direction. Interesting to note that in some areas the grains beneath the scale of sandblasted samples are equiaxed and have smaller size, as shown in Fig. 4.

The impedance diagrams for sandblasted samples preoxidised at 1100°C, Nyquist and Bode plots, are shown in Figs. 5 and 6, respectively. For comparative reasons, results for the samples at zero time are also included. Figure 5 shows straight lines which approach the real impedance axis as the treatment time is increased from 1 to 10 h. At the high frequency zone, the presence of a depressed semi-
circle is evident, specially for samples thermally treated for 10 h. For the longest exposure of 100 h a straight line, closer to the imaginary impedance axis, is observed. The Bode diagram of phase angle versus frequency (Fig. 6b) shows angle values between $-70^\circ$ and $-80^\circ$ at the highest frequencies for samples preoxidised at 1, 3 and 10 h. At the lowest frequencies a minimum is observed, for which the angle value diminishes with the treatment time. Sandblasted samples treated at 1 100°C for 100 h show a similar diagram to that obtained for the samples at zero time, but the angle values are higher.

The Nyquist and Bode impedance diagrams obtained for the polished samples preoxidised at 1 100°C for different exposure times are presented in Figs. 7 and 8, respectively. The Nyquist diagram of Fig. 7 shows capacitive arcs of variable amplitude for all treatment times. The trend to form a semicircle is higher for the samples heat treated for 1 h, which indicates the existence of a resistive component besides the capacitive behaviour. The Bode diagram of impedance modulus versus frequency, Fig. 8a), shows straight lines of slope $-1$ in the whole frequency range, independently of the treatment time. In the Bode diagram of phase angle versus frequency, Fig. 8b), there appear angle values around $-90^\circ$ in the whole frequency range. These values are typical of systems with a predominant capacitive component.

Comparing Figs. 6a) and 8a) it can be seen that the impedance modulus values at the lowest frequency for sandblasted samples are two orders of magnitude lower than those obtained for polished samples.

4. Discussion

An alternative to the use of bare metallic materials is the possibility of generating a ceramic coating by means of high temperature treatments in special alloys susceptible to generate such coatings.\textsuperscript{7,9} The high temperature treatment gives rise to the formation of a compact and continuous coating with a very good adherence, that hinders the anodic reaction due to the corrosion process in the metallic substrate. As a consequence, the metallic ion release to the physiological medium is suppressed and the toxic effects that they produce are avoided.

The ODS FeCrAl alloy treated at 1 100°C generates a dense $\alpha$-alumina layer,\textsuperscript{13} which should be inert to the surrounding tissues.\textsuperscript{14} The thickness of the layer varies as a function of treatment time and initial roughness of the metallic substrate (Fig. 3). This investigation has shown that sandblasting of the ODS FeCrAl alloy prior to the oxidation treatment at 1 100°C introduces microstructure differences with respect to the polished samples thermally oxidised under the same conditions (Fig. 4).

On the one hand, the more severe plastic deformation at the surface of sandblasted samples accounts for the formation of a fine-grained microstructure in the outer surface of
the samples by recrystallisation during heat treatment. This microstructure contrasts with the large and very elongated grains developed in the interior of the sample as a consequence of a secondary recrystallisation. This coarse microstructure is obviously similar to that observed for the polished samples after the thermal oxidation treatment. The presence of a fine-grained microstructure at the outer surface of the sandblasted samples could account for their lower scale thickness. In fact, it has been reported for other alloys that a decrease of the grain size increases the density of diffusion paths for the elements forming the scale. This feature enables the fast formation of the protective scale in the earlier stages of oxidation. It also may be advanced that the outer fine-grained structure might be advantageous for the mechanical behaviour of the preoxidised alloy. In a previous investigation it has been shown that the scale impairs the ductility at room temperature of the coarse-grained material by increasing the stress triaxiality state. Taken into consideration that the fracture initiation zone of preoxidised samples occurred just beneath the scale, and that a decrease of grain size in ferritic materials would decrease the ductile-brittle transition temperature, the presence of a small grain size at the outer part of the substrate could increase the mechanical performance of the preoxidised alloy.

On the other hand, sandblasted samples are prone to scale spallation than those generated on polished samples, specially for the samples with the 10 and 100 h of exposure. This feature is consistent with the more severe residual stress state as roughness and thickness of the scale increases.

A question still arises as to how far the surface modifica-
Corrosion behaviour of the preoxidised ODS FeCrAl alloy was evaluated in physiological solution considering these two variables: roughness of the metallic substrate and scale thickness. In order to analyse the different impedance diagrams obtained, the electrochemical equivalent circuit that appears in Fig. 9 has been proposed. $R_o$ is the ionic resistance of the electrolyte; $Q_{Al}$ represents the capacity of the alumina scale; $R_i$, is the ionic resistance of the alumina layer due to the ion migration transport through paths or microdefects of this layer allowing the connection between the electrolytic medium and the base material; $R_{tc}$ is the charge transfer resistance associated with the electrochemical process; and finally, $Q_{dc}$ represents the double layer capacity of the metallic substrate. The last one parameters, $R_{tc}$ and $Q_{dc}$, contribute only in the impedance diagrams when there is a connection between...
aggressive medium and metallic substrate through microdefects in the alumina layer.

Impedance diagrams for sandblasted samples treated for 1 and 3 h (Fig. 6) show lower impedance values at the lowest frequency (two orders of magnitude) than those in polished preoxidised samples (Fig. 8) for the same treatment times. Since scale spallation for these samples was not significant, other factors appear to influence the impedance diagram shape. The new contribution can be attributed to the presence of paths or fine cracks in the alumina layer that communicate the aggressive medium with the metallic substrate.

The impedance diagrams obtained for sandblasted samples treated for 10 h show clearly this new contribution. At the highest frequencies, a first depressed semicircle associated with the alumina coating ($R_e$ around $10^6 \Omega$) and a straight line or the beginning of a second semicircle of high amplitude assigned to the behaviour of the base material are obtained. It seems, therefore, that the integrity or the magnitude of microdefects increases with exposure time, according with previous results. At this treatment time, the magnitude of the microdefects can be so critical that residual stress can be sufficient to induce local spallation of the alumina layer. The depressed shape of the first semicircle in the Nyquist diagram is due to the surface heterogeneity of the sandblasted samples. This high surface heterogeneity causes a distribution of capacities, with different time constants, in which the admittance value is obtained by the following expression:

$$Q = jw^n Y_o$$

Where $Q$ is the admittance value; $w$, is the angular frequency; $n$, is the exponent with values between 0 and 1; and $Y_o$ is the apparent capacity. When $n$ is 0.5, the electrochemical response in the impedance diagram causes a distortion as that observed in the Fig. 6.

In sandblasted samples treated for 100 h is not possible to separate the contributions due to the alumina layer and the metallic substrate in the impedance diagram. This is due to the similar time constant obtained for both processes, so their contributions are jointly presented in the impedance diagram. From the above corrosion results is interesting to note that in the sandblasted samples treated for 10 and 100 h, where the spallation of the alumina layer is evident, the corrosion resistance is about two orders of magnitude lower compared to that of the polished samples. However, the corrosion resistance is typical of materials in a passive state and remains stationary along the immersion time.

The impedance diagrams for polished samples obtained in the Hank’s solution reveal that the applied signal is mainly inverted in charging and discharging the condenser formed by the alumina scale, $C_{Al}$. For that, the electrochemical response of the Nyquist diagram corresponds to a nearly pure condenser. The dielectric form of the alumina scale possesses a capacity whose value depends on the pre-oxidation time, $i.e.$, on the thickness. In Fig. 10 we show the variation of the capacity values as a function of the immersion time and preoxidation time at high temperature. The increase of the layer thickness provokes a decrease in the capacity, that is consistent with the expression:

$$C = \varepsilon_r \varepsilon A/d$$

Where $\epsilon_r$, is the vacuum permittivity; $\varepsilon$, the dielectric constant of the alumina; $d$, the thickness, and $A$, the tested surface area. The higher the treatment time, the higher the thickness value and the lower the capacity value.

The capacity values depend on the absorbent properties of the coatings. In the case of polymeric coatings, the capacity values increase with the immersion time due to the permeation of the coating. In our preoxidised ODS FeCrAl alloy, the capacity values remain constant with the immersion time (Fig. 10), indicating the high impermeability of the alumina coating. However, oxidised polished samples showed slight deviations from capacitive behaviour in the Bode phase angle diagram versus frequency (Fig. 8b), where phase angles lower than −90° were detected at high frequencies. These slight deviations are due to the presence of microdefects in the alumina layer. However, the magnitude of these microdefects is so small that the corrosion reaction is not produced.

5. Conclusions

(1) Alumina layer generated at high temperature on sandblasted and polished samples present a high chemical inertia as electrochemical techniques have revealed. In addition, a high impermeability of the alumina layer was inferred from the evolution of the capacity values with immersion time.

(2) Sandblasted samples have a relative lower oxidation rate than polished samples, as scale thickness measurements have indicated.

(3) Sandblasted samples are prone to scale spallation than polished samples, specially for the longer exposure times (10 and 100 h). However, the corrosion behaviour of oxidised sandblasted samples is good even when spallation occurs. In that cases, the corrosion behaviour is due to the contribution of both alumina layer and metallic substrate response.

(4) Preoxidised polished samples show a nearly pure
capacitive behaviour. The lower values of capacity are obtained for the highest thickness of the alumina layer.

(5) In preoxidised polished samples, the microdefects in the alumina layer manifested by the slight deviation in the phase angle of $\theta_{900}$ at high frequencies, do not increase with immersion time.

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