Behavior of Ti-6Al-4V surfaces after exposure to water disinfected with ionic silver

I. Mintsouli a, V. Tsiridis b, M. Petala b,*, N. Pliatsikas c, P. Rebeyre d, E. Darakas b, M. Kostoglou a, S. Sotiropoulos a, Th. Karapantsios a

a Department of Chemistry, Aristotle University of Thessaloniki, Thessaloniki, 54124, Greece
b Department of Civil Engineering, Aristotle University of Thessaloniki, Thessaloniki, 54124, Greece
c Department of Physics, Aristotle University of Thessaloniki, Thessaloniki, 54124, Greece
d ESA/ESTEC, P.O. Box 299, 2200 AG, Noordwijk, The Netherlands

A B S T R A C T

It is well documented that ionic silver prevents microbial proliferation in water systems, e.g., tanks and piping, reducing health risks and degrading of potable water quality. However, ionic silver interacts with wetted surfaces resulting in depletion of silver ions from water. This study investigates the loss of silver from water when in contact with titanium alloy Ti-6Al-4 V. Use of ionic silver in Ti-6Al-4 V water tanks is one of the options under consideration by National Aeronautics and Space Administration’s (NASA) for disinfection of potable water in future long term missions. The present tests resemble real conditions during storage in water tanks regarding the ratio of wetted surface area to liquid volume, silver ions concentration in water as well as temperature and light conditions. In all examined cases, silver ions vanish completely from the water and at the same time traces of vanadium and aluminium mitigate from the solid surface to the water. Extensive SEM and high resolution XPS analyses demonstrate that silver is present on the Ti-6Al-4V surface in its oxidized form (Ag⁺ and Ag⁴⁺). This could be explained either by the mechanism of galvanic deposition of metallic silver and its subsequent transformation to oxides or by an ion-exchange mechanism whereby silver ions are chemisorbed at negatively charged Ti-O- sites present on the surface of the Ti alloy. All present findings underline the potential risk of not achieving potable water quality standards when water is stored in Ti-6Al-4 V tanks.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

This study examines the depletion of ionic silver from potable water when water is stored in containers made of a Ti-6Al-4 V alloy. The purpose of this study is in line with the use of this material in the potable water storage tanks designed for future long term missions beyond the low-Earth orbit.

Commercially pure titanium (Ti) and its alloys are used in a wide range of aerospace, industrial and medical applications due to their excellent properties, such as high corrosion resistance, strength and light weight [1]. The excellent corrosion resistance of Ti and Ti alloys is due to the spontaneous formation of a tightly adhesive, stable and continuous oxide layer at their surface upon exposure to oxygen either in air or in water [2]. The most commonly used Ti-alloy, Ti 6Al-4 V, contains Al and V stabilizers that offer improved mechanical properties compared to commercially pure Ti and an excellent combination of high strength, light weight, formability and corrosion resistance properties [3]. Ti 6Al-4 V is highly resistant to general corrosion in aqueous solutions including seawater [4], as well as in oxidizing acids, chlorides (in the presence of water) and alkalis [1]. Therefore, Ti-6Al-4 V uses include heat exchangers, aircraft turbine engine components, aircraft structural components, aerospace fasteners, high-performance automotive parts and marine applications. In addition, Ti-6Al-4 V biocompatibility and reliability has promoted its use in biomedical applications, especially in orthopaedic ones. Despite the corrosion resistance of Ti-6Al-4 V, there are serious concerns related to biofouling (often followed by materials’ degradation) when Ti-6Al-4 V is in contact with water or other aqueous media [4,5].

Ti-6Al-4 V has also been selected as one of the primary materials of the water system storage of the Orion vehicle. Possible interactions between its wetted surface and water may degrade the quality of the latter, as explained below. Orion Multi-Purpose Crew Vehicle (MPCV) has been designed by National Aeronautics and Space...
Administration (NASA) for exploration missions beyond low-Earth orbit. Orion MPCV will carry the Orion service module, which is provided by the European Space Agency (ESA) and is designed for the storage of water, nitrogen and oxygen, among other duties [6]. Potable water is, after oxygen, the second consumable needed by crew members to live aboard a spacecraft and by far, the most critical with regards to mass. In the context of manned long term spaceflight missions, long shelf life for potable water is required. To this regard, prevention of microbial proliferation within the water systems is essential, in order to limit potential crew health risks. Control of microbial growth in the potable water supply systems is ensured by the addition of adequate amounts of biocidal molecules at production sites [7]. For future long term missions, ionic silver has been identified as the biocide agent of potable water [8]. Ionic silver has been acknowledged as an efficient disinfectant agent and is thoroughly investigated against numerous types of microbes, bacteria, viruses, protozoa, algae etc [9]. Among various advantages, silver can be safely consumed by humans, unless it is consumed at high concentrations for a long period of time [10].

Besides NASA's plans to use ionic silver in future long term missions, ionic silver is currently used as a preservative for potable water aboard the Russian segment of the International Space Station (ISS). So far, the European Space Agency (ESA) has successfully delivered potable water using ionic silver as biocide [7] aboard the Automated Transfer Vehicle (ATV). However, during the launch campaigns a fluctuation of silver was observed by performing water quality analyses at different steps of the water process during each campaign, implying possible water quality degradation [8,11]. The main type of metallic wetted surface of water storage tanks in that case has been Stainless Steel (SS) from the Ground Support Equipment (GSE) used for water transportation and loading. Indeed, there are few relevant studies found in literature, which show that silver depletion from bulk water might occur on SS depending on various factors, such as the wetted surface area to water volume ratio (S/V), type of wetted surface, etc [12,13]. Therefore, in view of the future long term missions and in order to ensure adequate potable water quality, it is of paramount importance to study possible interactions between biocidal ionic silver and Ti-6Al-4V and how these interactions are affected by several factors, such as S/V ratio, water storage conditions, etc. The understanding of the underlying phenomena may contribute to optimize water systems used aboard. Besides, such systems are also used in terrestrial applications, such as portable water purification (employed by military personnel, survivalists, and others for water purification when they need to obtain drinking water from untreated sources) [14] or drinking water disinfection for unprivileged societies [15].

Callahan et al. [12] and Roberts et al. [13] investigated the depletion of silver with regard to several materials compatible with potable water systems. These studies showed that the type of material and the type of surface treatment affected significantly the degree of ionic silver depletion from water. Russian water quality standards for cosmonauts/astronauts require the lower threshold limit for ionic silver to be 0.2 mg/L, and the higher acceptable concentration to be 0.5 mg/L, the latter corresponding to the initial silver concentration added into potable water during preparation [7]. In our previous work [16,17] we have also identified different behaviour of various types of wetted surfaces when in contact with water containing biocidal silver ions. During experiments with 0.5 mg/L initial concentration of silver at a S/V ratio equal to 5.0 cm⁻¹, silver was fully depleted from bulk water in all cases where the wetted surface was metallic. However, in experiments with initial concentration of silver equal to 10 mg/L, the degree of depletion from bulk water depended considerably on the type of wetted surface. Apart from tracing silver loss in bulk water, there has been also some SEM microscopic evidence for silver species deposition on metal specimens of materials used in potable water storage tanks and delivery piping (namely, stainless steel and Inconel alloys), following their contact with biocidal ionic silver solutions [12,13]. The same researchers suggested that the deposited silver was in its metallic form, based on EDS analysis of the identified deposits. Recently, Petala et al. [16] examined thoroughly the deposition of silver from aqueous solutions to SS surfaces using chemical analyses and X-ray Photoelectron Spectroscopy (XPS) and found evidence that silver deposits in its metallic form on all stainless steel surfaces, in line with a galvanic deposition mechanism. The latter entails metallic silver deposition-ionic silver reduction with simultaneous stainless steel substrate oxidation- involving Fe, Ni or Cr (components of stainless steel) oxide growth at the exposed surface.

This work is part of a project supported by ESA (European Space Agency) to examine the phenomena responsible for biocide concentration fluctuations in water systems for crew usage. ESA interest stems from the need to provide the ISS crew with potable water of long term chemical stability, in order to exclude any potential threat in crew health related to water quality degradation. The scope of this work is to investigate the decrease of biocidal ionic silver concentration in water exposed to Ti-6Al-4V and study the mechanism of silver deposition on this material. The former has been studied by water analysis (spectrophotometry and ICP-MS) while the latter has been approached by identifying the chemical state of silver deposits with XPS.

2. Materials and methods

2.1. Water preparation

Two types of water were synthetically produced: Water containing high silver concentration (10 mg Ag⁺/L), such as that employed currently to pre-condition the water storage tanks to be launched to the ISS, and water containing low silver concentration (0.5 mg/L) that refers to potable water quality according to Russian standards [7]. Synthetic water of each type was freshly prepared according to methods and standards described in previous studies [16,17].

2.2. Exposure of Ti-6Al-4V surfaces to water

Ti-6Al-4V flat strip coupons (Length x Width x Depth: 76 x 12.7 x 1.6 mm) were obtained from Metal Samples (Alabama, USA). Test coupons were exposed to water at surface to volume ratio (S/V) equal to 5.0 cm⁻¹. Total wetted surface area in the experiments was about 78 cm² of Ti-6Al-4V. The exposure period of Ti alloy to water containing 10 mg/L Ag⁺ ions was 7d, while the exposure period to water containing 0.5 mg/L Ag⁺ was 28d. The aforementioned specific durations of exposure were suggested by the European Space Agency as most suspected periods to observe variations in silver concentration. After meticulous cleaning of the test surfaces, according to JP5322.1G (NASA) and ASTM G1 protocols [18,19], four coupons were immersed in each well of a multiwell plate made of polypropylene (PP) (HJ-Bioanalytik, Germany) and treated as described elsewhere [16,17] at conditions shown in Table 1. Tests were implemented in triplicate, while in each series of tests, there was also a blank sample (without exposed metal) in order to examine possible deposition of silver on the polypropylene (PP) walls of the experimental container (multiwell plate). At the end of the exposure period, all water samples were subjected to silver concentration determination and to trace metals analysis. In addition, coupons were withdrawn from test wells and were dried inside a Plexiglas container under continuous nitrogen gas flow.
Table 1

<table>
<thead>
<tr>
<th>Experimental conditions</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface to volume ratio</td>
<td>5.0 cm⁻¹</td>
</tr>
<tr>
<td>Exposure period</td>
<td>7d (water with 10 mg/L Ag ions), 28d (water with 0.5 mg/L Ag ions)</td>
</tr>
<tr>
<td>Temperature</td>
<td>30 °C</td>
</tr>
<tr>
<td>Light conditions</td>
<td>Dark</td>
</tr>
</tbody>
</table>

At the end of the exposure period, all water samples were subjected to silver concentration determination and to trace metals analysis. In addition, coupons were withdrawn from test wells and were dried inside a Plexiglas container under continuous nitrogen gas flow. After drying, coupons were stored in PP tubes in nitrogen atmosphere. Some coupons were then subjected to leaching, in order to recover the silver deposited on their surface and be able to perform total silver mass balance. The rest of the coupons were subjected to microscopic analysis. The rest of the coupons were subjected to microscopic analysis. For leaching, 5N nitric acid solution was used as leaching medium. Leaching experiments were carried out in 50 mL PP tubes. Initially, the tubes were immersed into a heated ultrasonic cleaner and were sonicated for 30 min at about 60 °C. Then, the tubes were placed on an orbital shaker and were agitated at about 200 rpm for 24 h (room temperature). Afterwards, the test coupons were removed and leachates were subjected to chemical analysis for total silver determination.

2.3. Analysis methods

Silver was measured spectrophotometrically by using the LCK 354 method developed by Hach Lange. In addition, major cations, such as Ca²⁺, Mg²⁺ etc, as well as trace metals were analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

Auger electron spectroscopy (AES) and scanning auger microscopy (SAM) measurements were performed in an Axis Ultra DLD system (Kratos Analytical) using a 3 keV Field Emission electron beam for excitation. The energy resolution of analyser had ΔE/E ratio of 0.6%. AES spectra were acquired at 1 eV/step. The emitted Auger electrons were selected using a hemispherical energy analyzer and detected with a channeltron. The residual gas pressure in the vacuum chamber was not more than 7E-10 Torr. The studied surfaces were cleaned of adventitious carbon by using a 4 kV Ar⁺ ion beam; the same procedure was employed for sputter-etching of the sample in cases that an XPS depth profile was sought (a 20 s sputter time resulted in the removal of ca 1 nm of material). Data interpretation was performed with the Kratos-Vision software.

Table 2

<table>
<thead>
<tr>
<th>METAL ION</th>
<th>ION CONCENTRATION IN WATER WITH 0.5 mg Ag⁺/L INITIAL CONCENTRATION (mg/L)</th>
<th>ION CONCENTRATION IN WATER WITH 10 mg Ag⁺/L INITIAL CONCENTRATION (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BLANK</td>
<td>Water sample</td>
</tr>
<tr>
<td>Ag</td>
<td>0.48 ± 0.02</td>
<td>0.00</td>
</tr>
<tr>
<td>Al</td>
<td>&lt;0.002</td>
<td>&lt;0.002</td>
</tr>
<tr>
<td>Cr</td>
<td>0.0060 ± 0.0005</td>
<td>0.0002</td>
</tr>
<tr>
<td>Cu</td>
<td>&lt;0.002</td>
<td>&lt;0.002</td>
</tr>
<tr>
<td>Fe</td>
<td>&lt;0.002</td>
<td>&lt;0.002</td>
</tr>
<tr>
<td>Mn</td>
<td>&lt;0.002</td>
<td>&lt;0.002</td>
</tr>
<tr>
<td>Mo</td>
<td>&lt;0.002</td>
<td>&lt;0.002</td>
</tr>
<tr>
<td>Ni</td>
<td>0.0030 ± 0.0005</td>
<td>0.0003 ± 0.0005</td>
</tr>
<tr>
<td>Se</td>
<td>&lt;0.002</td>
<td>&lt;0.002</td>
</tr>
<tr>
<td>Ti</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>V</td>
<td>&lt;0.001</td>
<td>0.0224 ± 0.0005</td>
</tr>
</tbody>
</table>

3. Results and discussion

3.1. Water analysis

Test coupons made of Ti-6Al-4 V were exposed to water containing either 10 or 0.5 mg/L Ag⁺. At the end of the exposure period, chemical parameters of the water samples were examined, in order to evaluate the stability of water quality under the tested conditions. Table 2 presents the results of the measurement of metallic ions into water. In addition, the results of blank test water that was not brought in contact with Ti-6Al-4 V surfaces are reported for comparison reasons.

The results suggested strong depletion of silver ions from the water bulk in both types of tested water. In the case of potable water (initial Ag⁺ concentration of 0.5 mg/L) silver ions were completely depleted from water, while in the case of water with high silver concentration (10 mg/L) only 0.3 mg/L of silver ions were traced after only 7d of exposure period. This is in line with the findings by Wallace et al. [8] who charged water with organisms identified in ISS water samples and demonstrated that the biocidal efficacy of silver ions was reduced when water was stored in Ti vessels due to silver ions depletion.

Leaching of Ti-alloy coupons was used in order to verify the deposition of silver onto the solid surfaces. Moreover, the sum of the deposited silver mass on the solid surface and the container’s walls was compared to the sum of silver mass that was depleted from the water bulk and the silver mass that remained to the bulk after the test period, so as to corroborate the closure of silver mass balance. Table 3 shows the results of silver concentration determination in the leachates produced after leaching of the Ti-6Al-4 V coupons at the end of the test period. The results confirmed the deposition of silver onto the surfaces and demonstrated a strong potential of silver ions to migrate from the water to the solid surface. Moreover, calculations about the mass balance of silver indicated that only a small portion of silver ions are deposited on the walls of container,
while the largest the silver mass balance closed reasonably to a degree higher than 90%.

Regarding the rest of metals, traces of Al and V were detected into the water, at the end of the exposure period. (Note that, the dissolution of Al and V from the surface of Ti-6Al-4V coupons poses an additional possible threat for the degradation of potable water quality). However, the initial ionic content (gr-eqs) of water in silver ions is considerably higher than the resulting ionic content in AI and V ions, even if calculations involve the higher ionic states of these metals. This is evidence that the observed mitigation of Al and V from the solid surface to the water as dissolving ions cannot be quantitatively related with the much higher loss of ionic silver from the bulk water. In other words, the charge associated with Al and V ion formation cannot balance the charge that would be required for the reduction of Ag+ to metallic silver via a simple galvanic replacement mechanism. Hence, either silver is deposited as a metal via a more complicated galvanic deposition mechanism that involves the growth of Ti, Al and V oxides (as was the case of stainless steel-see Petala et al. [16]) or it is deposited in ionic form via an alternative mechanism.

3.2. SEM and Auger analysis

The above discussion means that, even though the deposition of silver onto Ti-6Al-4V was confirmed by the chemical analyses, the deposition mechanism could not be elucidated without further exhaustive microscopic and/or spectroscopic analysis of the solid surfaces.

SEM micrographs of a Ti-6Al-4 V coupon in a location not in contact with water, before Ar-sputtering of the surface, are shown in Figs. 1 and 2 respectively to set the background (silver-free sample) of microscopic analysis. Significant substrate roughness, due to a series of parallel ridges and sporadic craters, can be observed in Fig. 1; the rather obscured micrograph clarity is most likely due to adventitious carbon surface contamination (see also below).

Sputtering of the surface removes adventitious carbon and reveals the existence of brighter features (that could be either particles or splinters), as seen in Fig. 2.

The Auger spectrum at one of these features is shown in Fig. 3. High Ti peaks can be seen while the peak that could be associated with C is small with respect to that obtained at a non-sputtered sample (results not shown). These findings indicate that the bright features are not foreign particles but rather splinters/imperfections of the Ti substrate that were hidden (in terms of SEM imaging) before sputtering because of a surface covered by a C layer.

Fig. 4 shows a SEM micrograph of a Ti-6Al-4 V coupon that has been in contact with water containing 10 mg Ag+ /L, after it has been mildly Ar-sputtered (for 20 s, removing ca. 1 nm of material); it also presents a wide area Auger spectra onto a feature (splinter or possible particle) and out of it. The two spectra are almost identical. It should be noted that AES spectra taken before sputteriing-not
shown—were qualitatively similar to those obtained for sputtered samples.

A closer look into the silver peak energy range is provided by the spectra shown in Fig. 5, where also the effect of sputtering and results for a substrate feature not in contact with water are shown for comparison.

There is no detectable peak corresponding to silver for a sample location not in contact with Ag⁺-containing water, indicating that the small silver peak obtained at samples that have been treated with such water is not due to impurities. It is clear that no AES peak attributable to silver can be seen in Fig. 3 or in the corresponding spectrum (4th from the top) in Fig. 5. For samples in contact with water, silver could be detected on the sample’s surface by Auger spectroscopy both on and out of the bright features, excluding the possibility of the feature shown being silver particles. This finding is very important since it is a first indication that, unlike the work of Roberts et al. [19], silver deposits in our case are not in the form of large aggregates and hence cannot be identified by SEM. Finally, silver is detected even when 3 nm are Ar-sputtered off the surface, indicating that the deposits are thicker than 3 nm (see also sputter-etch XPS experiments below).

### 3.3. XPS analysis

In order to obtain a quantitative analysis of the surface of samples using a larger probed area and also to elucidate the chemical state of its components, XPS spectroscopy was employed. It confirmed the presence of silver on the outer surface layers of samples in contact with water, as can be seen in the wide area XPS spectra taken at 4 different spots and shown in Fig. 6: Ti, O and high C peaks are observed for the non-sputtered sample examined.
The compositional analysis data based on the obtained XPS spectra are given in Table 4. A small concentration variation among the 4 different spots has been found both for silver and the rest of the elements, however following no clear trend. This indicates that silver deposits over the entire specimen surface in contact with water.

In order to obtain depth profiling of the sample, gradual (1 nm/20 s) Ar-sputtering was applied for 60 s to the spot with the highest silver concentration (spot 4; 0.6% at.) resulting in a total of 3 nm removal from the surface in increments of 1 nm. Fig. 7 shows wide area XPS spectra before and after Ar sputter-etching of the surface. After sputtering, the C peak almost disappeared indicating almost total removal of surface contamination and the other peaks of the substrate (Ti, Al and V) became clearer. More precisely, Ti obtained its characteristic double peak instead of a triple peak mixed with oxides observed before sputtering, indicating the removal of the native oxide TiO₂ layer, while peaks due to Al and V are now clear/detectable.

From XPS spectra similar to those shown in Fig. 7 the atomic and mass percentage composition of the surface layers can be estimated as a function of distance from the outer surface and the results are given in Table 5. Also, atomic concentration depth profiles based on these data are shown in Fig. 8. The concentration of carbon becomes almost zero after the first 20 s of Ar-sputtering confirming the removal of a carbon contamination layer typically of 1 nm thickness. The silver concentration increases after the first 20 s of Ar-sputtering (due to gradual C removal) and then remains almost constant indicating that silver is deposited as films or islands of a thickness higher than 3 nm. (Note however that no safe silver film thickness estimation can be made by XPS sputter-etch data in this case because of significant surface roughness of the substrate and of an uneven deposit.) One may also note the surface depletion of the sample from V and the near constancy of Al concentration.

In order to probe the composition deeper into the sample, Ar-sputter-etch XPS experiments were repeated on a different location, sputter-etching a significant number of surface layers. Atomic concentration depth profiles obtained after gradual sputtering of 51 nm of material are shown in Fig. 9. Silver concentration is 0.62% in the beginning, gets its maximum value (1.26%) after 160 s of sputtering (removing 8 nm of the surface) and then slowly decreases. In the end (after 51 nm were removed), silver concentration is 0.45%. (Note again that this doesn’t necessarily represent silver film thickness because of significant surface roughness of the substrate and of an uneven deposit.)

Information about the chemical state of silver in the outer layers of the sample was obtained by narrow area, high energy resolution XPS spectra of a gradually sputtered Ti-6Al-4 V sample in the Ag 3d binding energy region; these are shown in Fig. 10. After Ar sputtering, the silver peaks are more intense but no shift to binding energies of metallic silver [20,21] is observed (unlike the situation
Table 5

<table>
<thead>
<tr>
<th>Peaks</th>
<th>0 s (0 nm off)</th>
<th>20 s (1 nm off)</th>
<th>40 s (2 nm off)</th>
<th>60 s (3 nm off)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Atomic conc.%</td>
<td>Mass conc.%</td>
<td>Atomic conc.%</td>
<td>Mass conc.%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag 3d</td>
<td>0.6</td>
<td>3.71</td>
<td>1.15</td>
<td>4.24</td>
</tr>
<tr>
<td>C 1s</td>
<td>55.48</td>
<td>37.92</td>
<td>5.34</td>
<td>2.19</td>
</tr>
<tr>
<td>O 1s</td>
<td>32.94</td>
<td>29.99</td>
<td>50.99</td>
<td>27.85</td>
</tr>
<tr>
<td>Ti 2p</td>
<td>9.52</td>
<td>25.93</td>
<td>36.2</td>
<td>59.16</td>
</tr>
<tr>
<td>Al 2p</td>
<td>1.29</td>
<td>1.98</td>
<td>5.4</td>
<td>4.98</td>
</tr>
<tr>
<td>V 2p</td>
<td>0.16</td>
<td>0.47</td>
<td>0.91</td>
<td>1.59</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.1</td>
<td>1.79</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.97</td>
<td>2.99</td>
</tr>
</tbody>
</table>

Fig. 10. XPS spectra of a gradually sputtered Ti-6Al-4V coupon in the Ag 3d binding energy region.

Fig. 11. XPS spectra of a Ti-6Al-4V coupon in the Ag 3d binding energy region before and after sputtering off 8 and 16 nm.

for silver deposited on stainless steel). According to literature data [22-24] the peaks located at 367.3 eV and 373.3 eV respectively can be associated with Ag⁺ and Ag⁹⁺ states (such as those reported in the literature for AgO oxides, a mixture of Ag₂O and Ag₂O₃).

Information about the chemical state of silver inner layers was obtained after the removal of 8 nm (where silver concentration is maximum according the previous experiment) and finally after 16 nm sputtering (where most of the elements concentrations have stabilized). Fig. 11 shows high resolution, XPS spectra of the sample’s surface before and after sputtering off 8 and 16 nm. Silver atomic concentration moves from 0.95% to 3.12 and 2.17% respectively. Ag 3d peaks are again located at 367.3 eV and 373.3 eV confirming that even the core silver isn’t in its metallic form on a Ti-6Al-4V coupon.

The results of Figs. 10 and 11 mean that, unlike stainless steel substrates, silver is present in its oxidized forms Ag⁺ and Ag⁹⁺ on Ti-6Al-4V. Thus, it is either deposited in ionic form (possibly bound on O-containing surface groups—see also below) or originally deposited as metallic silver (via a galvanic deposition mechanism that involves silver ion reduction and substrate oxide growth) and subsequently transformed to Ag₂O and Ag₂O₃ oxides by oxygen spillover from oxygen-rich Ti, Al and V.

The presence of silver on the Ti-6Al-4V in an ionic form could be explained by an ion-exchange mechanism, whereby positively charged Ag ions are bound by the negatively charged native oxide surface of TiO₂ (at pH = 8 TiO₂ carries a net negative charge due to the acidic dissociation of surface OH groups); similar interpretation has been given for increased Ca²⁺ uptake by Ti substrates [25].

4. Conclusions and further work

(i) Biocidal silver in ionic form was completely depleted from space mission quality water when in contact with Ti-6Al-4V surfaces.

(ii) Silver was present in its oxidized form (Ag⁺ and Ag⁹⁺) on the Ti-6Al-4V surface. This could be explained either with the galvanic deposition of metallic Ag and its subsequent transformation to oxides or by an ion-exchange mechanism whereby Ag ions are chemisorbed at negatively charged Ti-O⁻ sites present on the surface of the Ti alloy at pH = 8.

(iii) Distinguishing between the two mechanisms would involve prolonged experiments at increasing silver ion water concentration, whereby the galvanic deposition mechanism would involve continuous silver depletion whereas the ion-exchange mechanism would lead to surface saturation once the ion-exchange capacity of the surface is exhausted.

Acknowledgements

This study was carried under the program “Biocide Management for Long Term Water Storage” funded by ESA (Co. No. 4000109529/13/NL/CP). The view expressed herein can in no way be taken to reflect the official opinion of the European Space Agency. The authors gratefully thank Professor P. Patsalas and Professor G. Vourlias, for helpful discussions regarding XPS issues.

References


[18] International Space Station Medical Operating Requirements Document, JSC 50260. In NASA Johnson Space Center, 2003, Revision B.


