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INTERFACIAL REACTIONS BETWEEN TITANIUM AND BORATE GLASS

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ABSTRACT

Interfacial reactions between the melts of several borate glasses and titanium have been investigated by analytical scanning electron microscopy (SEM) and by x-ray photoelectron spectroscopy (XPS). A thin titanium boride interfacial layer is detected by XPS after short (30 minutes) thermal treatments. ASEM analyses after longer thermal treatments (8-120 hours) reveal boron-rich interfacial layers and boride precipitates in the Ti side of the interface.

INTRODUCTION

Titanium and titanium alloys have a number of attractive properties, including outstanding strength-to-weight ratios and excellent corrosion resistance, which make them desirable materials for a variety of aerospace and biomedical applications. The use of titanium as a component alloy, however, is limited by the lack of a reliable glass/Ti sealing technology. Conventional silicate glasses readily react with Ti when sealed to form an interfacial silicide layer [1-3]. This weakly adhered layer significantly reduces the mechanical strength of silicate glass/Ti seals [3] and precludes coating titanium alloys with silicate-based bioactive glasses for prosthetic applications [4].

Borate glasses have been recently shown to form strong bonds to titanium and titanium alloys [3,5] and to improve the adhesion of bioactive glasses to titanium [4]. Borate glasses can be prepared with a wide range of thermal and chemical properties for different packaging applications. Little is known, however, about the high temperature interfacial reactions between these glasses and titanium.

EXPERIMENTAL PROCEDURE

A variety of different borate glasses have been examined, including B_2O_3 and a barium aluminoborate composition (in mole%, 40BaO 20Al₂O₃ 40B₂O₃) with a nominal thermal expansion match to titanium [for details, see refs. 3,5]. Reaction couples for analytical scanning electron microscopy were prepared from cups and lids, machined from commercially pure titanium (grade 2, 99+%), each enclosing a 6 mm diameter, 2 mm thick glass disk. Each couple was sealed in an evacuated (1 mTorr) silica ampule and heat treated for various times and temperatures, depending on glass composition. After heat treatment, the reaction couple was removed from the ampule, cross-sectioned perpendicular to the Ti/glass interface, mounted in epoxy, and polished to a one-micron diamond finish. The interfaces were observed with an optical microscope and then a scanning electron microscope (SEM). Where a reasonable amount of interface was observed, wavelength dispersive spectrometer (WDS) mapping for each of the elements in the diffusion couple was undertaken. A Pb-STE crystal was used for the light element B and O analysis. X-ray maps, 256 x 256 pixels were obtained for each element with a dwell time of 0.2 sec per pixel. A beam

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voltage of 15 kV and a beam current of ~100 nA was used. The high beam current was used to increase the x-ray count rate for B and O, although some contamination of the specimen surface occurred.

A number of axial seals were also made between 10 mm diameter aluminoborate or commercial silicate (Kimble Glass TM-9) glass rods and titanium, each joined after 30 minutes in an argon-atmosphere furnace. The aluminoborate glass seals were formed at 670°C and the silicate seals at 950°C. These seals were fractured in air at the glass/metal interface and both interfaces were examined by x-ray photoelectron spectroscopy (XPS). Binding energies have been referenced to the C1s peak at 284.8 eV for adventitious carbon.

RESULTS AND DISCUSSION

The axial seals made between titanium and silicate glass could be easily separated by hand at the glass/metal interface, whereas the aluminoborate glasses adhered much more strongly to the titanium. These latter seals usually fractured in the glass, several millimeters from the titanium interface. These observations are in qualitative agreement with the finding that titanium pin seals made with aluminoborate glass withstand nearly twice the load before failure than do comparable seals made with silicate glass [3].

Figure 1 shows a Si2p photoelectron spectrum collected from the titanium side (upper trace) and the glass side (lower trace) of a silicate glass/titanium axial seal. The Si2p (~99 eV) and Ti2p_{3/2} (453.6 eV, not shown) binding energies of the species on the Ti-side of this failed seal are typical of those reported for Ti-silicide thin films [6]. An interfacial silicide, most likely Ti₅Si₃ [2], results from the reduction of the SiO₂ component of the glass:

TiO₂ (gl) represents the Ti³⁺/Ti⁴⁺ ions that dissolve into silicate glass sealed to titanium [1-3]. The poor adherence of silicate glass to the interfacial silicide contributes to mechanically weak glass/Ti seals [2,3] and to the poor bonding of dental porcelain to Ti [7] and to the poor

Figure 1: Si2p spectra of the two surfaces of a fractured axial seal between Ti and a silicate glass

Figure 2: B1s spectrum of the Ti-side of an axial seal to an aluminoborate glass.

adherence of Ti-thin films to fused silica substrates [8].

Comparable reduction reactions occur when borate glasses are sealed to titanium. Figure 2 shows the Bls spectrum collected from the Ti side of an axial seal with a barium aluminoborate glass. These samples fractured in a much different manner than axial seals made with silicate glasses. Most of the titanium interface remains bonded to a glass layer several millimeters thick. The residual glass has a binding energy of ~ 192 eV. However, a second Bls peak at ~ 187 eV is associated with a reduced phase that is also adhered to the titanium. This latter binding energy is typical for metal borides [9].

The Ti-boride interfacial reaction product that forms under normal sealing conditions (e.g., 670°C for 10-30 minutes) is too thin to be detected by SEM. (In comparison, the Ti-silicide interfacial layer is $>1\text{ }\mu\text{m}$ thick after sealing a silicate glass for ten minutes at 950°C [3]). To identify the composition of this interfacial phase and to study its formation, glasses were reacted with Ti for up to 120 hours to yield sufficient reaction product for study by SEM.

Figure 3a shows a back scattered electron image of the interface between the barium aluminoborate glass and Ti after reaction for 120 hrs at 800°C . The glass has crystallized but remains adhered to the titanium, despite cracking. Precipitates can be seen extending up to $10\text{ }\mu\text{m}$ into the titanium. The B x-ray map (fig. 3b) of this interface shows the boron-rich interfacial layer adhered to the Ti as well as the boron-rich precipitates in the Ti. Figure 4 shows the backscattered electron images of much larger precipitates extending over $40\text{ }\mu\text{m}$ into the titanium from the interface of a $1000^{\circ}\text{C}/16\text{ hr}$ reaction couple with the barium aluminoborate glass. Similar Ti-B reaction products were noted at the interfaces of couples to B_2O_3 and lanthanoborate glasses. With the possible exception of lanthanum-containing precipitates (not shown), no other glass cations are concentrated in the interfacial reaction products.

Very little is known about the thermochemical equilibria and kinetics of reactions between B_2O_3 and Ti. Preliminary thermochemical calculations

Figure 3: a) Backscattered electron image of the interface between a barium aluminoborate glass and Ti reacted at 800°C for 120 hours; b) the B x-ray map of the same area

Ti

Figure 4: Backscattered electron image of the interface between a barium aluminoborate glass and Ti reacted at 1000°C for 16 hours.

of the B-O-Ti-Ar system have been done with the computer program SOLGASMIX [10] using the thermodynamic properties of potential reaction products listed in the JANAF tables [11]. At 973 K and 1 atm (conditions that simulate the environment used to prepare the aluminoborate/Ti axial seals), TiB_2 is a thermodynamically stable reaction product only when the oxygen partial pressure (p_{O_2}) is $<10^{-33}$ atm; higher oxygen partial pressures oxidize the titanium and precludes reduction of B_2O_3 . This p_{O_2} is well below that estimated for the graphite furnace ($\sim 10^{-18}$ atm) used to prepare the axial seals that exhibit an interfacial Ti-boride. This suggests that the local environment of the glass/Ti interface is significantly more reducing than the furnace atmosphere. The dissolution of oxygen into Ti at the reaction interface may be one mechanism for lowering the local p_{O_2} .

West et al. [4] report the formation of crystalline $TiBO_3$ as the result of the reaction between molten B_2O_3 and Ti. Using this phase to represent Ti^{3+} dissolved into the glass, one possible interfacial reaction that yields TiB_2 is:

$TiBO_3 (gl)$ represents the Ti^{3+} and/or Ti^{4+} ions that dissolve into the borate glass [3]. The thin borate glass layers that remain adhered to titanium when axial seals are fractured are usually discolored, suggesting that Ti^{3+} is present in the glass. The actual stoichiometry of the interfacial boride is, at present, unknown. The Ti-B phase diagram [12] suggests that TiB , Ti_3B_4 , and TiB_2 are possible stoichiometries. Quantitative electron microanalysis of these reaction products are currently in progress.

The wavy interfaces of the glass/Ti reaction couples (Figs. 3 and 4) are characteristic of dissolution reactions. It thus appears that a titanium boride phase nucleates at the interface after an initial dissolution of Ti into the glass. Longer times and higher temperatures cause precipitates to grow because of the concomitant diffusion of boron from the glass into the titanium.

The development of an interfacial boride reaction product does not adversely affect the adherence of borate glass to titanium, in contrast to the well-known deleterious effect of silicide formation on the adherence of silicate glasses. This may be related to the relative kinetics of the two reactions. Considerably thicker silicide phases form when silicate glasses are reacted than the boride interfacial phases that form when borate glasses are sealed using comparable times and temperatures. As a result, the silicate seals are more susceptible to tensile stresses that would develop from possible thermal contraction and elastic moduli mismatches between the glass, the titanium, and the interfacial phases. The relative reaction kinetics and their effects on seal performance are currently under study.

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