OXIDATION OF Al-CONTAINING AUSTENITIC STAINLESS STEELS

AS RELATED TO THE FORMATION OF STRONG GLASS-CERAMIC TO METAL SEALS

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ABSTRACT

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Glass-ceramic to metal seals are used in pyrotechnic actuators and ignitors. Metals that have been successfully demonstrated for this application include several nickel-based alloys and a family of Al-containing austenitic stainless steels. Seals made between a lithia-alumina-silica (LAS) glass-ceramic and nickel-based alloys show excessive metal attack by the glass. This is also true of the Al-containing alloys but the etching action of the glass is less severe. This attack will cause reactions to occur at the glass-ceramic/metal interface. Not all reactions are detrimental to the seal, but some are and these unwanted reactions can cause the formation of pores and the subsequent loss of hermeticity. In this paper, LAS glass-ceramic will be sealed to Al-containing alloys that were first oxidized prior to sealing-called 'preoxidation'. Results will be given that show 'preoxidation' of the alloys substantially reduces the probability of glass/metal reactions during seal formation. The reduction in the amount of reaction products that are created improves the overall quality of the interface without loss of seal bond strength. In addition, the mechanism of surface oxide formation on these Al-containing steels is discussed. Auger data are presented that show the composition of the resulting oxides to be a function of the oxidation temperature. There are two theories that exist on the mechanism of oxidation; one is that oxidation occurs at the air/oxide interface (Abderrazik, et al, 1987) and the other is that oxidation takes place at the oxide/metal interface (Hindam and Smeltzer, 1980). In order to study which theory is correct for the Al-containing alloys, oxidation of the alloys were performed, first in pure $^{16}\text{O}_2$, and then followed by pure $^{18}\text{O}_2$. Secondary ion mass spectroscopy (SIMS) imaging results showed no layered structure but did show a mixture of oxides. Thus, the mechanism of oxidation of these alloys is not simple and must be occurring in such a manner as to allow oxygen to have access at all stages of the oxidation process.

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Production of a glass-ceramic to metal seal in the manufacture of pyrotechnic actuators and ignitors is the most critical step in the processing of these devices. During use, these devices give rise to gases which are at a high temperature and pressure. The magnitude of the observed temperature and pressure is dependent on the particular application. Thus for these uses, a strong and hermetic seal between the metal and the glass-ceramic is required. Control of several parameters is necessary to meet the strength and hermeticity requirements. The parameters to be controlled include the strength of the metal, the strength of glass-ceramic, the match in the coefficient of thermal expansion (CTE) between the two, and the magnitude of the bond strength between the metal and the glass-ceramic. Seals are routinely made at Mound between a nickel-based alloy, Inconel-718, and a lithia-alumina-silica (LAS) glass-ceramic. However, because nickel-based alloys are higher in cost, more difficult to machine, and generally more difficult to weld when compared to iron-based alloys, alternative material sets have been sought. One such set is a family of Al-containing austenitic stainless steels. These steels form non-spalling alumina films which protect the base metal from excessive oxidation⁽¹⁾.

The process of oxidizing a metal prior to its sealing to glass is a widely used method to passivate the metal and subsequently improve the glass to metal seal. Pask⁽²⁾ has shown that an oxidized metal surface provides the necessary chemistry to achieve a good bond. Al-containing stainless steels used in our study can form, under certain oxidation conditions, stable aluminum oxide, Al_2O_3 , surface films. However, Al_2O_3 films are not always formed. Thus, one of the goals of this study was to establish the minimum conditions which would allow for the formation of alumina films on Al-containing stainless steels. Auger spectroscopy was utilized in exploring the oxide composition as a function of oxidation temperature. In addition, secondary ion mass spectroscopy (SIMS) data will be presented which will explain the mechanism of oxide formation.

Previous authors have shown that alumina is compatible and soluble in LAS-glass to at least ten percent.⁽³⁾ We have previously shown that these glasses produce strong and hermetic seals when bonded to the Al-containing stainless steels.^(4,5) This work will demonstrate that the seal quality can be improved, and without loss of bond strength, by 'preoxidizing' the alloy to form a non-spalling alumina film prior to sealing with the LAS glass-ceramic.

EXPERIMENTATION

Three Al-containing alloys^(*), 880, 896, and 899, were used in this study. These alloys have approximately the same composition. The primary difference is in the relative amount of aluminum. Specifically these alloys have the following compositions (in wt%): 880: Al-4.77, Cr-9.7, Ni-24.5, Mn-0.14, Zr-0.026, Y-0.094, and Fe-Bal; 896: Al-4.15, Cr-10.6, Ni-22.1, Mn-0.2, Zr-0.10, Y-0.10, and Fe-Bal; and 899: Al-5.2, Cr-10.6, Ni-20.9, Mn-0.21, Zr-0.10, Y-0.10, and Fe-Bal. 'Doughnut' shaped coupons (Figure 1) of the 880 alloy were cut from 1/4" diameter tubing. The thickness of each sample was approximately 1/16". A ceramic crucible was used to hold the samples inside a stainless steel container. The flanges were sealed with copper gaskets (see Figure 1), and the sample container was then attached to the oxygen transfer system (see Figure 2). The system was pumped with a 170 l/sec turbomolecular pump to a vacuum of less than 0.007 Torr. With the pump isolated from the vacuum system, $^{16}\text{O}_2$ was backfilled into the sample container with two atmospheres of gas pressure. The container was then isolated from the transfer system via a pinch weld and placed in a muffle furnace and heated to 1000°C for six hours. The container was cut open and the sample rings were removed. A new container was assembled into which these sample were loaded, and the process repeated with $^{18}\text{O}_2$. These two oxidation processes yielded six samples of the alloy 880 that were first oxidized with $^{16}\text{O}_2$ followed by oxidation with $^{18}\text{O}_2$.

A representative sample from the $^{16}\text{O}/^{18}\text{O}$ oxidized alloy was polished at a very sharp angle, $<10^\circ$, so as to accentuate the oxide layer and make it easier to analyze with imaging SIMS. An initial investigation showed that the polished cross-section had a layer of carbon, therefore, the sample was lightly sputtered. Following this sputtering an oxide was found which was appropriate for imaging SIMS.

(*) Obtained from Hoskins Manufacturing Company, Hamburg, MI

The instrument used in the SIMS study was a modified MA500 Auger microprobe fitted with a MIG300 30keV Gallium liquid metal ion gun and an MML2-12S quadrupole with a HTO-2000 ion optics head. The optics were operated at zero extraction voltage to facilitate acquisition of positive and negative ion images with minimum image lateral shift. Three images were recorded at a 30 micron field of view; the images were of ^{16}O , ^{18}O and Al measured from the oxidized surfaces.

Other coupons of the 880 alloy were also oxidized in air as follows: 5 hours at 600°C , 3 hours at 700°C , 90 minutes at 800°C , and finally 15 minutes at 1075°C . A sample of alloy 899 was oxidized in air at 1200°C for 2 hours, as well. These samples were analyzed by Auger spectroscopy.

Auger spectra were taken on a Perkin-Elmer Physical Electronics, Model #4100 Thin film Auger electron spectrometer which is interfaced with a Perkin-Elmer 7500 microcomputer for data acquisition. Typically, the electron beam was rastered over an area of $\sim 500 \text{ microns}^2$ with a beam energy of 5 keV and a beam current of ~ 0.5 microampere. Scans were an average of ~ 20 spectrum sweeps; the analysis time was ~ 20 minutes. Sputtering for in-depth elemental profiles was done with two Perkin-Elmer, Model #04-303 ion guns. The area sputtered is $\sim 1 \text{ mm} \times 1.2 \text{ mm}$ oval area for a 3.5 keV beam energy. A typical sputtering rate for a chemical vapor deposited silicon nitride standard⁽⁶⁾ at 3.5 keV is about 700 Å/min total for both guns.

Hydrostatic burst testing was performed on glass-ceramic/Alloy 896 seals. This testing has been described in detail elsewhere.⁽⁷⁾ A total of twelve seals were made; six with the as-received alloy and six with an alloy that was oxidized for 3 hours at 1000°C prior to sealing. The burst strengths were measured to be 4020 ± 290 psi and 3980 ± 320 psi, respectively. The metal wall thicknesses were 0.035".

A metal/glass-ceramic seal was also made between the 896 alloy and the IAS glass-ceramic. The IAS glass-ceramic composition is (in wt%): 75- SiO_2 , 12.3- Li_2O , 4.7- Al_2O_3 , 1.2- K_2O , 2.5- P_2O_5 and 1.3- B_2O_3 . A sealing/crystallization cycle without the precipitation hardening step was used to make the seal.⁽⁸⁾ This sample was cross-sectioned, mounted and polished. Negative backscattering electron images were performed on a JEOL 733 superprobe.

Figures 3a through 3d show Auger in-depth elemental profiles produced from the air oxidation of the 880 Al-containing alloy and Figure 3e shows the depth profile of air oxidized Al-containing alloy 899. The temperatures of oxidation were 600, 700, 800, 1075 and 1200°C, respectively. Each profile was recorded on a specimen that was oxidized at a different temperature for a different length of time. For samples that gave rise to the data in Figures 3a through 3d, the time was varied so as to produce oxides of approximately the same thickness. The oxide that produced Figure 3e was intentionally made thicker. The profiles show the composition of the resultant oxide to be dependent on the temperature at which the oxidation was performed. The oxides that were formed up to and including 800°C show a two-layered structure. The outside layer was found to be rich in aluminum, iron and chromium oxides, whereas the inner layer was alumina. As the temperature of oxidation increased the concentration of the aluminum in the outside layer increased, until at 1075 °C there is only one layer, aluminum oxide. The Auger profile at 1200°C (Figure 3e) supports this finding. Zaizen et al⁽⁹⁾ has also shown the results of the oxidation of similar Al-containing stainless steels to be a mixed oxide on the alloy surface. Their oxidation was performed at 1200 °C. They also found a two-layered system similar to our results for steels containing ~5 wt% Al and less than 15 wt% Cr. They observed iron and chromium oxides in the external aluminum oxide layer, a finding not observed by us in the Auger profiles of the 899 alloy that was oxidized at 1200°C.

The formation of a surface aluminum oxide on an Al-containing alloy could be produced by one of two ways: the first is the migration of a reduced state of aluminum to the surface, and the second is the diffusion of oxygen through the oxide layer and into the bulk. The first mechanism would involve oxidation occurring at the oxide/air interface⁽¹⁰⁾ and the second involves oxygen diffusion through the passivation layer such that oxidation would be occurring at the metal/oxide interface⁽¹¹⁾. Figures 4a through 4c illustrate SIMS images of $^{16}\text{O}^-$, $^{18}\text{O}^-$ and Al^+ , respectively, for the 880 Al-containing alloy which was oxidized first by $^{16}\text{O}_2$ and then second by $^{18}\text{O}_2$. As can be seen from the images, the oxide layer is fragmented and indistinct, and is not a clear continuous layer. The images also show many ribbon-like features; the ribbons generally lie perpendicular to the outer surface and contain high concentrations of oxygen and aluminum. Oxidation progresses along defects in the

ality structure, most probably along the grain boundaries (or "O" pathways-see Figure 4) in the alloy. Since ^{18}O and ^{16}O are both seen in the fragmented oxidized layer along the 'O' pathway, it is difficult to conclude which oxidation mechanism is occurring. Since the $^{18}\text{O}^-$ image (Figure 4a) is broadened along the "O" pathways, this suggests that the oxidation is selectively occurring at the air/oxide interface. However, it appears that the oxygen has access to mix along these pathways. Eldridge et al⁽¹²⁾ have studied the thermal oxidation of an aluminum single crystal with $^{18}\text{O}_2$ at 550°C by SIMS profiling. They monitored the AlO^- species and found strong evidence for oxygen anion transport, proceeding, first with the exchange of ^{18}O with ^{16}O from the Al_2O_3 outerlayer, and second by oxidation below this outerlayer. Eldridge's work supports our study, suggesting that the oxidation occurs at the air/oxide boundary in the "O" pathways, followed by lateral growth of the oxide into the metal.

Sealing a glass to a metal results in an interface that shows metal attack (see Figure 5a). This metal attack^(4,5,13,14) gives rise to an etched metal surface, a reaction zone containing phosphide precipitates (the black dots in Figure 5a), a diffusion zone containing a few wt% chromium, and a glassy phase with less devitrified crystals that exhibits a lower thermal expansion than either the metal or the glass-ceramic. Upon sealing to the 896 Al-containing alloy that had first been 'preoxidized', the resultant interfaces show very little metal attack (see Figure 5b), very small reaction and diffusion zones, no glassy phase, and a general overall improvement in the quality of the seal. In addition, glass-ceramic/metal bond strengths for 896/LAS glass-ceramic seals were determined on as-received and 'preoxidized' metals. The results showed no detrimental effect on the strength of the seal following 'preoxidation'. Therefore, 'preoxidation' of Al-containing alloys prior to sealing should be considered as a viable technique to be used in making pore-free and strong seals for cryotechnic applications.

CONCLUSIONS

In this paper one or more of the Al-containing alloys were: 1) oxidized in air (specifically alloys 880 and 899) in order to determine the surface oxide composition for various oxidation temperatures; 2) sequentially oxidized (specifically alloy 880), first with $^{16}\text{O}_2$ then followed with $^{18}\text{O}_2$ to study the mechanism of oxidation; 3) sealed (alloy 896) to IAS glass-ceramic for interfacial examination and burst strength determinations; and, finally 4) 'preoxidized' and sealed (alloy 896) to the glass-ceramic again for interfacial and burst strength measurements. The analytical techniques that were used include Auger electron spectroscopy, secondary ion mass spectroscopy (SIMS) and backscattered electron imaging. The Auger results showed the surface oxide composition to vary with oxidation temperature. At temperatures below 1075°C a two-layer structure was found to form, an outer-layer composed of oxides of Fe, Cr and Al and an inner-layer of alumina. At 1075°C this two layered structure was noted to merge into a single one consisting of only alumina. The SIMS results revealed an oxidation process that occurs along "O"-pathways, most probably grain boundaries, but also occurs in such a manner that oxygen is able to mix along the oxidation path. Negative backscattered images of cross-sectioned and metallographically polished IAS glass-ceramic/alloy 896 seals showed improved interfacial quality for seals made where the alloy was first 'preoxidized'. These seals made with 'preoxidized' alloy 896 also showed no loss in bond strength. Therefore, in the future seals made with IAS glass-ceramics and Al-containing alloys, 'preoxidation' will be considered.

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List of Figures

Figure 1. Stainless Steel Sample Container with "Doughnut" Shaped Coupons.

Figure 2. Oxygen Transfer System Showing Pump, Isolation Valve, Pressure Gauge and Oxygen Gas Bottle.

Figure 3. Auger In-Depth Elemental Profiles of Oxides Produced at: a) 600° for 5 hr, b) 700° for 3 hr, c) 800° for 90 min, d) 1075° for 15 min, and e) 1200°C for 2 hr. The First Four Samples Were Made with Alloy 880 and the Last Sample with Alloy 899.

Figure 4. SIMS Images for: a) $^{16}\text{O}^{-}$, b) $^{18}\text{O}^{-}$, and c) Al^{+} of $^{16}\text{O}_2/^{18}\text{O}_2$ Oxidized Al-Containing Alloy, 880. Sample Was Polished at a Very Sharp Angle to Accentuate the Surface Oxidation.

Figure 5. Negative Backscatter Electron Images of Interfaces Made by Sealing LAS Glass-Ceramic to Alloy 896 for: a) As-Received and b) 'Preoxidized' Metals.

'Doughnut'
Shaped
Sample

Ceramic
Crucible

Sample
Container

To Oxygen
Transfer →
System

Pressure
← Gauge

→
To Sample
Container

←
Isolation
Valve

Oxygen
Gas Bottle

← 170 l/sec
Turbo-
molecular
Pump

KEY

- ▲ O
- Cr
- ★ Fe
- ◆ Ni
- | Al