Chemistry of Glass-Ceramic to Metal Bonding for Header Applications

I. Effect of Treatments on Inconel 718
and Hastelloy C-276 Metallic Surfaces

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Abstract

Auger electron spectroscopy and depth Auger profiling were used to study the surfaces of Inconel 718 and Hastelloy C-276. The metal surfaces were processed in the same manner as is presently being used in the manufacturing of glass-ceramic headers. At each step in the process, samples were studied with Auger spectroscopy to determine their resultant elemental surface composition and film thickness. In addition, the effect of a final plasma cleaning operation on the metal surface was examined. The results show that the type and concentration of surface species and the thickness of the surface oxides are dependent on the processing technique.

Introduction

The fabrication of glass-ceramic headers for use in initiators and actuators is a complex manufacturing process, the ultimate success of which is dependent on the quality of the glass-ceramic to metal seal [1,2]. The seal must have certain properties, such as hermeticity and burst strength, to ensure the successful function of the header. Glass-ceramic headers usually consist of: a high tensile strength shell, one to several metal rings or pins that act as electrical feedthroughs, and a glass-ceramic that functions as the electrical insulator. In the most recent headers the glass-ceramic to metal seals have been fabricated using a lithia-alumina-silica glass and either Inconel 718 or Hastelloy C-276 as the metal piece parts. To study the change in the surface chemistry caused by the different manufacturing processes on the metal surfaces, Auger electron spectroscopy was employed. A better understanding of each process treatment is necessary so that the glass-ceramic parts can be improved according to programmatic needs.

Experimental

Sample preparation

Because it was the nature of this investigation to evaluate subsequent surface treatments, an unusual amount of time and effort was expended in the preparation of the different samples. Hence, the surface preparation will be described in some detail.

Two different alloys, Inconel 718 and Hastelloy C-276, were selected for study during the course of this work. These materials have relatively high tensile strengths and are corrosion resistant [2]. Because of these properties, these materials are presently being used in the fabrication of certain glass-ceramic headers for use in several weapon components. For this application the materials can function either as electrical feedthroughs or as the main structural member. The chemical compositions of these nickel-based alloys [3] are listed in Table 1.

Sample specimens were prepared by cutting discs 1/16 in. thick from 1/4 in. rod stock using a high concentration

Table 1 - CHEMICAL COMPOSITIONS OF TWO NICKEL-BASED ALLOYS SELECTED FOR STUDY

	Inconel 718		Hastelloy C-276	
	wt %	at. %	wt %	at. %
C	0.04	0.2	0.01	0.05
Mn	0.09	0.09	0.4	0.40
Sr (max.)	0.2	0.1	0.08	0.06
Cr	17.8	19.8	15.6	18.9
Ni	50.2	49.4	57.1	61.2
Co	-	-	1.6	1.7
Mo	2.80	1.7	15.3	10.1
W	-	-	4.1	1.4
Fe	22.0	22.8	5.4	6.1
Nb	5.18	3.2	-	-
Ti	0.93	1.1	0.20	0.3
Al	0.64	1.4	-	-
Cu	0.13	0.1	0.15	0.13
P	<0.008	<0.017	<0.01	0.019
Sn	<0.05	<0.10	<0.02	0.04

diamond wafering blade mounted on a Vari/Cut low-speed saw, Model No. VC-50.* Saw speed was around 7 m/min and Isocutt Fluid** was used as the lubricant. The slow cutting speed and the use of the lubricant ensured that the samples were not heated during the cutting operation. Approximately 25 samples of each alloy were cut. Following being cut, the samples were sealed in a jar until selected for the different surface treatments to be discussed below.

Figure 1 shows a schematic of the experimental design that was used during the

*Manufactured by Leco Corporation, St. Joseph, Michigan.

**Buehler Ltd., Evanston, Illinois.

course of this work. This schematic illustrates the different sequences of surface treatments that were followed. All of the samples were initially cleaned using a four-step cleaning operation. This is basically used as a degreasing procedure. The specified sequence used in this surface preparation is shown in Table 2. The four-step cleaning solution consists of 80% by volume of isopropyl alcohol, 20% by volume of distilled demineralized water (~15 MΩ), 0.2% by volume of Triton N-101, and 0.5% by volume of Span 80. (See Appendix for information on Triton and Span.). After the four-step cleaning operation, three specimens of each alloy were sealed in jars while the others were sent to the next surface treatment.

FIGURE 1 - Experimental design flow sheet.

Table 2 - FOUR-STEP
CLEANING PROCESS

1. Ultrasonically clean in methylene chloride (2 min).
2. Ultrasonically clean in four-step cleaning solution.
 - 80% by volume isopropyl alcohol, 20% by volume distilled water.
 - Demineralized water (~ 15 m Ω), 0.2% by volume of Triton N-101, and 0.05% by volume of Span 80 (2 min).
3. Rinse in distilled demineralized water and ultrasonically clean in distilled water (1 min).
4. Ultrasonically clean in isopropyl alcohol (1 min).
5. Dry under heat lamp (minimum 15 min).

The next treatment is the sealing operation. This operation involves a heating

cycle typically used during the fabrication of glass-ceramic headers. The operation serves a two-fold purpose: 1) it melts the parent glass to form a glass-to-metal seal, and 2) it controls the formation of the glass-ceramic from the parent glass. To study the effect of this operation on the surface characteristics of the alloys alone, this processing step was performed without any parent glass. The sealing furnace (~ 1 ft³) used a tungsten mesh element for heating. The sealing cycle was performed under an argon atmosphere whose flow was high enough to allow complete gas replacement 20 times per hr. The complete sealing cycle is presented in Table 3. After the sealing cycle was completed, three samples of each alloy were placed in sealed jars while the

others continued to the next surface treatment. From Figure 1 it can be found that the remaining samples were next subjected to one of two different oxide removal treatments. The procedure outlined in Table 4 is commonly performed on headers to remove the surface discoloration that develops on the alloys following the sealing cycle. This is done to ensure that a good weld can be made to the different alloys. Again, once this procedure was completed, three samples of each alloy were stored in sealed jars while the others continued to the next surface treatment.

Table 3 - SEALING CYCLE^a

Ramp (°C/min)	Set Point (°C)	Soak (min)
100	1000	15
-50	660	15
30	800	30
-30	720	120
-30	620	120
-5	400	--
-2	100	--
Free Cool		

^aStarting from room temperature.

At this point the 50-min oxide removal samples were split up into three groups. One group underwent an argon plasma surface cleaning while the other two groups were exposed to two different oxygen plasma surface treatments. In plasma cleaning, gas is excited to an ionized state by the application of radio frequency power. The radio frequency power is applied externally to the sample chamber, which is under a weak vacuum, to produce a highly reactive plasma at low temperature operating conditions. The complete unit consists of a reaction

Table 4 - OXIDE REMOVAL

1. Add 68.8 g of NaOH to 125 ml of H₂O and stir.
2. Continue stirring and add 6.9 g of KMnO₄ while heating to 94°C.
3. When solution reaches 94°C, stop stirrer.
4. Place parts in solution for 50 min. (One study was made with parts left in contact with the solution for only 2.5 min.)
5. Remove parts and water rinse.
6. Place parts for 90 sec in a solution of 50% by volume of H₂O and 50% by volume of HCl.
7. Remove parts and rinse several times in water.
8. Dry under heat lamp.

chamber, radio frequency power supply, and a vacuum system. The choice of gas, wattage, and time determines the surface reactions that will occur and hence determines the surface treatment. The specific parameters used during the three plasma surface treatments are shown in Table 5. Again, each group of samples was exposed to only one set of plasma surface treatment parameters. After each group was processed the specimens were placed in sealed jars.

The samples from all of the different surface treatments were then prepared for analysis by Auger spectroscopy. The 2.5 min oxide removal samples were

Table 5- METHODS OF PLASMA CLEANING

Gas	Pressure (torr)	Power (W)	Time (hr)
Argon	0.5	200	0.5
Oxygen	0.5	200	0.5
Oxygen	0.5	200	2

treated with an electropolishing process. Electropolishing, or reverse electroplating, is the process of smoothing a metal surface anodically in a concentrated acid or alkaline solution. During the process, the products of anodic metal dissolution react with the electrolyte to form a film at the metal surface. This film is removed and reformed as the anodic process proceeds (as current is passed). The ultimate result is a metal surface that is smoother because the microprojections have been removed faster than the micro-depressions. Next, concentrated H_3PO_4 was used at 150°F in a polishing action. Parts from which oxide had been removed were placed in the H_3PO_4 bath and current was passed at $\sim 250 \text{ A/ft}^2$ of piece-part surface area for $\sim 90 \text{ sec}$. They were then rinsed in distilled water, submerged in HNO_3 for 90 sec, and finally rinsed again in distilled water. Auger analysis was performed on the sample.

Auger analysis

Auger analysis was performed on the above prepared coupons with a Perkin-Elmer, Physical Electronics, Model 545 Scanning Auger Microprobe (SAM). The Model 545 is mounted on a Varian Auger/-Leeds bell jar. Up to 30 samples can be mounted at one time. The system is roughed with two sorption pumps, packed with molecular sieve material of $\sim 5 \text{ \AA}$ pore size. The main ultrahigh vacuum (UHV) chamber has available three types of pumps: a) a titanium/molybdenum alloy sublimation pump, b) a 1000 L/s helium cryogenic pump, and c) a 200 L/s ion pump. A typical operational vacuum during the recording of surface scans was 1×10^{-9} torr. Auger scans were recorded with the primary electron beam set at 6 kV and $\sim 1 \text{ \mu A}$ sample current.

These conditions correspond to an electron beam size of $\sim 20 \text{ \mu m}$. Overall 5 min scans were taken with a 6-V peak-to-peak modulation voltage. Several Auger surface scans were taken on each treatment; a minimum of one and a maximum of 12 scans were recorded on any one.

Depth profiles were accomplished with a differentially pumped ion gun. This ion gun is the Mini-beam I Model manufactured by Kratos. Argon was allowed to flow into the rear of the ion gun.

An argon ion target voltage of 3 kV and a current of 50 nA were used in generating the in-depth elemental profiles. The diameter of the ion beam was $\sim 300 \text{ \mu m}$. The ion beam was rastered over an area of 600 by 600 $\text{\mu m}$ or $3.6 \times 10^{-3} \text{ cm}^2$. This corresponds to an ion current density of $13 \text{ \mu A/cm}^2$ and a sputtering rate on vapor-deposited Si_3N_4 films of 30 $\text{\AA/min}$.

Results and discussion

The results of the Auger analysis on the two different nickel-based alloys were examined. Inconel 718 and Hastelloy C-276 are discussed separately in the following sections.

Inconel 718 surface scans

A typical Auger surface scan on Inconel 718 that had been treated with the four-step cleaning procedure (as outlined in Table 2) is shown in Figure 2a. The scan shows that the remaining surface following the four-step cleaning is a mixed oxide surface of nickel, iron, and chromium (also possibly manganese). Contaminants of carbon, nitrogen, chlorine, and sulfur can also be seen. A trace of copper is also noticeable. Most probably the carbon and nitrogen (and possibly sulfur) contaminants are

FIGURE 2a - Auger surface scan on Inconel 718 after four-step cleaning.

the remains of a surfactant in Span or Triton which has concentrated on the surface of the Inconel 178. The origin of the sulfur could be the Isocutt Fluid, which was used as a lubricant in the specimen cutting operation. The chloride contaminant could be from one of three sources, chloride residuals left in the water, methylene chloride, or cutting fluid that had chemisorbed to the freshly cut metal surface.

The Auger surface scan of the Inconel 718 following sealing (see Table 3) is shown in Figure 2b. The scan shows that the sealing operation: a) causes increased surface oxidation, b) causes

titanium, aluminum, and manganese surface oxide enrichment, c) leaves the surface depleted in iron and nickel, d) shows an overall decrease in chlorine surface contamination and e) leaves a CrO_xC_y -rich surface. Depth profiles shown later in this report also show niobium enrichment near the surface after sealing. The titanium, aluminum, and manganese found present on the surface after sealing are most probably due to the migration of these elements from the bulk of the Inconel. This surface enrichment can most likely be attributed to the large free energy change (or gettering properties) for reactions shown on Table 6.

Table 6 - STANDARD STATE FREE ENERGIES OF FORMATION PER MOLE OF O_2 AT 1400 K

Reaction	$\Delta G_{1400 \text{ K}}$ (kcal/mole O_2)
$2 \text{ Ti} + \text{O}_2 \rightarrow 2 \text{ TiO}$	-196.017
$4/3 \text{ Ti} + \text{O}_2 \rightarrow 2/3 \text{ Ti}_2\text{O}_3$	-181.918
$4/3 \text{ Al} + \text{O}_2 \rightarrow 2/3 \text{ Al}_2\text{O}_3$	-195.992
$\text{Ti} + \text{O}_2 \rightarrow \text{TiO}_2$	-162.527
$2 \text{ Nb} + \text{O}_2 \rightarrow 2 \text{ NbO}$	-138.195
$2 \text{ Mn} + \text{O}_2 \rightarrow 2 \text{ MnO}$	-134.833
$4/5 \text{ Nb} + \text{O}_2 \rightarrow 2/5 \text{ Nb}_2\text{O}_5$	-124.262
$4/3 \text{ Cr} + \text{O}_2 \rightarrow 2/3 \text{ Cr}_2\text{O}_3$	-121.621
$2 \text{ Fe} + \text{O}_2 \rightarrow 2 \text{ FeO}$	-86.713
$\text{Mo} + \text{O}_2 \rightarrow \text{Mo} + \text{O}_2$	-81.848
$3/2 \text{ Fe} + \text{O}_2 \rightarrow \text{Fe}_3\text{O}_4$	-79.796
$4/3 \text{ Fe} + \text{O}_2 \rightarrow 2/3 \text{ Fe}_2\text{O}_3$	-73.68
$2 \text{ Ni} + \text{O}_2 \rightarrow 2 \text{ NiO}$	-55.6
$4 \text{ Cu} + \text{O}_2 \rightarrow 2 \text{ Cu}_2\text{O}$	-32.525
$2 \text{ Cu} + \text{O}_2 \rightarrow 2 \text{ CuO}$	-20.218

FIGURE 2b - Auger surface scan on Inconel 718 after four-step cleaning and sealing.

To a first approximation, these free energy changes (Table 6) can be used as an indication of the surface concentration if diffusion is very rapid at 1000°C for metal and oxygen and the rate of oxidation of surface metal atoms is the limiting factor. The most negative free energy changes of about the same magnitude are for titanium and aluminum and these elements are found on the surface. However, chromium is not predicted to be on the surface at 1000°C and its presence indicates that kinetic factors, such as diffusion rates, are of importance at 1000°C. These data at 1100°C indicate chromium depletion at the surface with aluminum and titanium the dominant metal components. In this case, thermodynamic factors appear to control surface composition.

Table 1 indicates that titanium and aluminum are present in bulk Inconel 718 in small quantities, 1.1 and 1.4 at. %, respectively. The concentration at the surface is at least a factor of 10 greater for these two elements, indicating diffusion to the surface. The driving force for this enrichment appears to be the oxidation of titanium and aluminum according to free energy changes as shown on Table 6.

Figure 2c illustrates the Auger surface scan following the $\text{KMnO}_4/\text{NaOH}$ oxide removal step for 50 min, then ~90 sec contact with 6N HCl (see Table 4 regarding details on the solution composition and treatment). It is obvious from the scan that increased surface contamination of calcium, potassium, sodium, sulfur, and chlorine results from the oxide removal step. These contaminants are most likely from the oxide removal bath that remained behind even after rinsing several times with demineralized water.

It is also obvious that the TiO_2 is removed in this step, but not the Al_2O_3 . Also, the CrO_xC_y surface has changed to an iron, chromium, nickel (manganese) oxide surface.

The Auger surface scans that followed the oxide removal step with three plasma treatments are shown in Figures 2d, 2e, and 2f. They represent, respectively: 1/2-hr treatment with argon plasma (2d), 1/2-hr treatment with O_2 plasma (2e), and 2-hr treatment with O_2 plasma (2f). The argon plasma treatment can be seen to reduce the carbon contamination, but still leaves the surface contaminated with amounts of sulfur, chlorine, calcium, sodium, and aluminum. O_2 plasma treatment shows the surface to be depleted in iron and chromium; in fact, no detectable chromium could be noted after 1/2 hr of O_2 plasma treatment. Also the iron concentration was found to decrease with increasing time of plasma treatment. The resultant surface following O_2 plasma treatment is mainly NiO with some Fe_2O_3 and a high level of Al_2O_3 contamination.

Another technique for removing the oxide left on the surface of Inconel 718 following the oxide removal step is a reverse electroplating, or electropolishing, step. A representative Auger surface scan following electropolishing is shown in Figure 2g. This scan shows that the major component left on the electropolished surface is NiO (29% Ni and 28% O). A large amount of carbon (22%) could also be detected, with lesser amounts of chromium (6%), nitrogen (5%), iron (3%), titanium (2%), sodium (2%), and traces of niobium. These data show an appreciable phosphorus signal. The amount of aluminum is barely detectable.

FIGURE 2c - Auger surface scan on Inconel 718 after four-step cleaning, sealing, and oxide removal.

FIGURE 2d - Auger surface scan on Inconel 718 after four-step cleaning, sealing, oxide removal, and argon plasma treatment for 1/2 hr.

FIGURE 2e - Auger surface scan on Inconel 718 after four-step cleaning, sealing, oxide removal, and oxygen plasma treatment for 1/2 hr.

FIGURE 2g - Auger surface scan on Inconel 718 after four-step cleaning, sealing, oxide removal, and electroplating.

Table 7 summarizes the Auger surface scan data taken on the various surface treatments given Inconel 718. The first column lists the elements and the second, the Auger line energies that were monitored during this study. The sensitivity factors in the third column were obtained from the "Handbook of Auger Electron Spectroscopy" published by Perkin-Elmer Physical Electronics Division [5] using the data available in the Handbook for a primary electron beam energy of 5 kV. The data summarized in Table 7 are given in atomic percent but are to be treated only as semi-quantitative. Data in parentheses are the standard deviations. In general, relative changes within the data can be taken as significant if, when comparing the results of two different treatments, the changes are >10%.

Inconel 718 depth profiles

Figure 3 comprises the ten depth Auger profiles taken after: (3a) and (3a') Treatment 1, four-step cleaning; (3b) and (3b') four-step cleaning plus Treatment 2, sealing; (3c) and (3c') four-step cleaning, sealing, plus Treatments 3 and 3', oxide removal for 50 min and 2.5 min, respectively; (3d) four-step cleaning, sealing, oxide removal for 50 min, plus Treatment 4, argon plasma treatment for 1/2 hr; (3e) four-step cleaning, sealing, oxide removal for 50 min, plus Treatment 5, O₂ plasma treatment for 1/2 hr; (3f) four-step cleaning, sealing, oxide removal, plus Treatment 6, O₂ plasma treatment for 2 hr; (3g) four-step cleaning, sealing, oxide removal for 2.5 min, plus Treatment 7, electropolishing. These results were generated using an argon ion beam superimposed on the primary electron beam such that the peak-to-peak intensity of each element could be continuously monitored during ion etching. The

data show the oxide layer on Inconel 718 following the four-step cleaning to be very thin. The time required to reduce the oxygen surface concentration to 50% of its maximum value ($t_{0.5}$) for the four-step cleaning shown in Figure 3a was determined to be 1.0 min; the time required to reduce oxygen to 90% ($t_{0.9}$) was found to be 2.6 min. Five such determinations were made. The average value for these ion etching profiles on oxygen was determined to be 1.1 min for $t_{0.5}$ and 2.7 min for $t_{0.9}$. These data are summarized in Table 8.

Assuming that the thickness of the oxide resulting from the four-step solvent cleaning is the same as that of a native, room-grown oxide (which is ~20 Å), the sputtering rate of the argon ion etching can be calculated to be 8 Å/min for 90% oxide removal. This sputtering rate can be used in estimating the thickness of resulting oxides in succeeding processes, however, oxides of different compositions can argon ion etch at different rates. For example, Al₂O₃ that is oxidized in air is known to sputter at 1/8 the rate of V₂O₅ [6]. With this limitation clearly in mind, oxide thicknesses ($d_{0.9}$) for the various surface treatments on Inconel 718 can be calculated. These have been summarized in Table 9.

The results to be discussed hereafter assume that the oxides resulting from the various surface treatments have similar sputtering rates. The conclusions that can be drawn, then, from the data in Table 8 or 9 are that the sealing operation: 1) increases the native oxide thickness by a factor of 15; and 2) leaves the surface high in concentrations of titanium, aluminum, chromium, oxygen, and carbon, most probably in the form of a chromium oxycarbide. These

Table 7 - SUMMARY OF DATA FROM AUGER SURFACE SCANS ON INCONEL 718

Element	Auger Energy (eV)	Sensitivity Factor ^b	Amount of Element ^a Removed by Various Surface Treatments (at. %)						
			1	2	3	4	5	6	7
			Four-Step Cleaning	Sealing	Oxide Removal	Argon Plasma	Oxygen Plasma 1/2 hr	Oxygen Plasma 2 hr	Electro-Polishing
S	150	0.74	0.39 (0.04)	0.2	1.4 (0.3)	4.0 (0.9)	2.9 (0.1)	0.6 (0.2)	0.4
Cl	180	1.03	0.74 (0.14)	0.24 (0.06)	0.93 (0.41)	0.6 (0.4)	0.3 (0.1)	0.4 (0.2)	0.2
K	250	0.9	0.19 (0.07)	0.24 (0.10)	0.44 (0.48)	<1.0	1.0	<0.9	0.3
C	270	0.14	32.3 (1.2)	33.8 (2.6)	23.6 (6.6)	7.8 (3.4)	6.9 (2.0)	9.0 (2.0)	22.0
Ca	292	0.42	<0.4	<0.2	1.6 (1.2)	1.6 (0.8)	1.1 (0.6)	<0.9	0.3
N	380	0.22	5.4 (0.9)	--	--	--	--	--	4.9
Ti	418	0.32	--	8.4 (0.7)	1.4 (0.7)	0.8 (0.4)	0.9 (0.1)	1.2 (0.5)	1.6
O	510	0.42	24.1 (1.0)	32.6 (2.1)	24.3 (1.1)	32.0 (4.0)	34.0 (0)	37.0 (4.0)	28.0
Cr	530	0.31	5.2 (0.1)	4.1 (0.5)	3.0 (1.3)	4.3 (0.7)	0.9 (0)	0.9 (0.1)	6.0
Mn	590	0.24	<0.8	1.2 (0.5)	<0.3	<1.0	<0.8	<0.5	<0.5
Fe	650	0.22	6.6 (0.3)	<0.8	1.5 (0.6)	3.5 (0.7)	3.7 (0.2)	<2.0	2.6
Ni	850	0.26	18.1 (0.4)	0.74 (0.33)	7.9 (1.8)	11.1 (1.7)	17.5 (0.3)	18.2 (3.0)	29.0
Na	990	0.25	<0.7	0.86 (0.12)	4.8 (0.6)	8.7 (3.0)	2.5 (0.2)	5.0 (7.0)	2.0
Mg	1175	0.14	<1.0	<1.0	1.1	1.5 (0.6)	1.1 (0.4)	<1.0	0.7
Al	1390	0.075	<4.0	15.5 (0.6)	29.0 (10.0)	22.0 (6.0)	27.0 (1.0)	21.0 (12.0)	1.3
Mo	220	0.28							
Co	775	0.24							
Nb ^c	167	0.22							
No. of Measurements			10	4	6	5	3	3	1

^aStandard deviation given in parentheses.
^bFrom Reference 5
^cNot calculated, but observed in some spectra.

FIGURE 3a - In-depth Auger elemental profile on Inconel 718 after four-step cleaning.

FIGURE 3a' - Repeat under different sputtering conditions of the in-depth Auger elemental profile on Inconel 718 after four-step cleaning.

FIGURE 3b - In-depth Auger elemental profile on Inconel 718 after four-step cleaning and sealing at 1000°C.

FIGURE 3b' - Repeat under different sputtering conditions of the in-depth Auger elemental profile on Inconel 718 after four-step cleaning and sealing at 1000°C.

FIGURE 3c - In-depth Auger elemental profile on Inconel 718 after four-step cleaning, sealing, and oxide removal with $\text{KMnO}_4/\text{NaOH}$.

FIGURE 3c' - Repeat under different sputtering conditions of the in-depth Auger elemental profile on Inconel 718 after four-step cleaning, sealing, and oxide removal with $\text{KMnO}_4/\text{NaOH}$ for 2.5 min.

FIGURE 3d - In-depth Auger elemental profile on Inconel 718 after four-step cleaning, sealing, oxide removal, and argon plasma treatment for 1/2 hr.

FIGURE 3e - In-depth Auger elemental profile on Inconel 718 after four-step cleaning, sealing, oxide removal, and oxygen plasma treatment for 1/2 hr.

FIGURE 3f - In-depth Auger elemental profile on Inconel 718 after four-step cleaning, sealing, oxide removal, and oxygen plasma treatment for 2 hr.

FIGURE 3g - In-depth Auger elemental profile on Inconel 718 after four-step cleaning, sealing, 2.5-min oxide removal, and electropolishing at 5A for 2 min 20 sec.

Table 8 - SUMMARY OF DEPTH AUGER PROFILING DATA FOR THREE ELEMENTS

Surface Treatment	No. of Measurements	Measurement Averages ^a (min)					
		Carbon		Oxygen		Chromium	
		t _{0.5}	t _{0.9}	t _{0.5}	t _{0.9}	t _{0.5}	t _{0.9}
1	5	0.5	1.4	1.8	4.4		
		0.5	1.2	1.0	2.5		
		0.8	2.2	0.8	1.8		
		0.4	1.2	1.0	2.6		
		0.6	1.2	0.9	2.1		
		0.6 (0.2)	1.4 (0.4)	1.1 (0.4)	2.7 (1.0)		
1,2	2	0.4	1.0				
		1.0	3.5	21.5	38.6	8.3	15.0
		0.7	2.2	12.0	20.0	21.5	28.0
		12.0	30.0	16.8	29.3	14.9	21.5
		26.5	35.0				
		19.2	32.5				
1,2,3,4	3	0.2	3.5	1.3	11.2		
		0.2	2.0	1.4	9.5		
		0.6	1.0	1.8	12.8		
		0.3 (0.2)	2.2 (1.4)	1.5 (0.3)	11.2 (1.7)		
1,2,3,5	1	0.4	1.8	20.5	50.0		
1,2,3,6	2	2.5	9.0	15.2	27.7		
		0.5	7.2	11.2	22.3		
		1.5	8.1	13.2	25.0		

^aStandard deviation given in parentheses.

Table 9 - SUMMARY OF DEPTH PROFILING OXIDE THICKNESS DATA^a

Surface Treatment	Approximate Thickness (Å) Measured at 90%
1	(20)
1,2	230
1,2,3	1800
1,2,3,4	100
1,2,3,5	400
1,2,3,6	200
1,2,3'	240
1,2,3',7	10

^aAssuming oxide on four-step solvent cleaned Inconel 718 is 20 Å.

conclusions can be made by comparing the ion etching times required to remove 90% of the oxygen Auger intensity, before and after sealing.

The following conclusions can be drawn by comparing the data from Figures 3a, 3b, and 3c: 1) the sputtering time necessary to remove 90% of the oxygen from the surface increases in the following order: 3a, 3b, 3c (2.7, 29.3, 225 min), and thus, the oxide removal step of 50 min produces a thicker oxide; and 2) the oxide stoichiometry is different before and after oxide removal for 50 min. The titanium oxide and the oxycarbide of chromium following the "sealing" process are indeed removed by the $\text{KMnO}_4/\text{NaOH}/\text{HCl}$ solutions in the

oxide removal step. However, an Al_2O_3 -rich surface is left on Inconel 718 following contact with the oxide removal solution.

Figure 2g shows the depth profile after electropolishing. The oxide surface is very thin and appears to be thinner than the oxide treated only by four-step cleaning. This can be attributed to the fact that the surface polishing action removes the microprojections faster than the microdepressions of the microrough Inconel 718 that has been four-step cleaned.

After an argon plasma treatment for 1/2 hr (Figure 3d) following oxide removal, the oxide thickness is immediately noticeably reduced. In fact, the oxide following exposure to the argon plasma is within seven times the thickness of the four-step cleaned oxide.

Hastelloy C-276

As shown in Table 1, Hastelloy C-276 has increased levels of the following elements as compared to Inconel 718: molybdenum (from 1.7 to 10.1%), cobalt (from 0 to 1.7%), tungsten (from 0 to 1.4%), manganese (from 0.09 to 0.4%) and nickel (from 49.4 to 61.2%). Significant decreases can be noted in iron (from 22.8 to 6.1%) and in niobium (from 3.2 to 0%). Other elements that showed reduction in elemental concentrations are titanium and aluminum. In this section, the data recorded on the surface chemistry resulting from the various surface treatments on Hastelloy C-276 will be compared to those data discussed in the previous section on Inconel 718.

Figures 4 and 5 illustrate typical surface scans and in-depth elemental profiles, respectively. Hastelloy C-276

following sealing is predominantly chromium oxide with significant amounts of aluminum and very little other surface contamination, whereas the surface of Inconel 718 following sealing, as discussed in the previous section, has an outermost layer consisting of oxides of titanium, aluminum, niobium, and chromium.

The results of "oxide removal" treatment on Hastelloy with alkaline KMnO_4 solution are shown in Figures 4c and 5c. The oxide removal treatment leaves the Hastelloy surface contaminated with sodium, calcium, and potassium and also results in a surface that contains both nickel and chromium oxides. This surface is very similar to that obtained in Inconel 718 following oxide removal except that the in-depth profile on the "oxide removed" Hastelloy surface (Figure 5c) shows a very thin oxide that is equal in thickness, that is $\sim 16 \text{ \AA}$, to the four-step solvent-cleaned oxide. This result is very much different from that found on the Inconel specimens undergoing similar processes; with the Inconel specimens the resultant oxide thickness was found to be 40 times that of the Hastelloy "oxide removed" surface.

Figures 4d to 4f and 5d to 5f illustrate the result of plasma cleaning the "oxide removed" Hastelloy C-276 specimens with an argon plasma for 1/2 hr (d), oxygen plasma for 1/2 hr (e), and oxygen plasma for 2 hr (f). The argon plasma cleaning leaves a surface rich in nickel and chromium oxides and containing small amounts of sulfur and chlorine. The oxide thickness is on the order of that of the native oxide. The O_2 plasma treatments enrich the surface in nickel oxide, reduce the overall general

FIGURE 4a - Auger surface scan on Hastelloy C-276 after four-step cleaning.

FIGURE 4b - Auger surface scan on Hastelloy C-276 after four-step cleaning and sealing at 1000°C.

FIGURE 4c - Auger surface scan on Hastelloy C-276 after four-step cleaning, sealing, and an alkaline KMnO_4 oxide removal treatment.

FIGURE 4d - Auger surface scan on Hastelloy C-276 after four-step cleaning, sealing, oxide removal, and argon plasma treatment for 1/2 hr.

FIGURE 4e - Auger surface scan on Hastelloy C-276 after four-step cleaning, sealing, oxide removal, and oxygen plasma treatment for 1/2 hr.

FIGURE 4f - Auger surface scan on Hastelloy C-276 after four-step cleaning, sealing, oxide removal, and oxygen plasma treatment for 2 hr.

FIGURE 5a - In-depth Auger elemental profile on Hastelloy C-276 after four-step cleaning.

FIGURE 5c - In-depth Auger elemental profile on Hastelloy C-276 after four-step cleaning, sealing, and an alkaline $KMnO_4$ oxide removal treatment.

FIGURE 5b - In-depth Auger elemental profile on Hastelloy C-276 after four-step cleaning and sealing at 1000°C.

FIGURE 5d - In-depth Auger elemental profile on Hastelloy C-276 after four-step cleaning, sealing, oxide removal, and argon plasma treatment for 1/2 hr.

FIGURE 5e - In-depth Auger elemental profile on Hastelloy C-276 after four-step cleaning, sealing, oxide removal, and oxygen plasma treatment for 1/2 hr.

FIGURE 5f - In-depth Auger elemental profile on Hastelloy C-276 after four-step cleaning, sealing, oxide removal, and oxygen plasma treatment for 2 hr.

surface contamination, and thicken the surface oxide coating. These are results similar to those observed with Inconel specimens that received similar plasma treatments.

Summary

The following surface treatments were given to two nickel based superalloys, Inconel 718 and Hastelloy C-276. The treatments were: 1) four-step solvent cleaning, 2) four-step cleaning followed by a high temperature sealing process, 3) four-step cleaning and sealing followed by an alkaline KMnO_4 plus HCl acid "oxide removal" step, and 4) four-step cleaning, sealing, and oxide removal followed by an argon plasma treatment, an oxygen plasma treatment, or an electropolish (on Inconel 718). The changes in the surface chemistry of Inconel 718 and Hastelloy C-276 superalloys caused by the various treatments were followed by Auger electron spectroscopy and depth Auger profiling. The following are the major conclusions:

1. The four-step cleaning process leaves the surface of both superalloys passivated with a native oxide consisting of predominantly nickel, chromium, and iron (and also possibly manganese in Inconel and molybdenum and manganese in Hastelloy); in addition, the oxidized surface is covered with a few monolayers of carbon and is also contaminated with sulfur, chlorine, and nitrogen.
2. The high temperature sealing operation leaves the surface of the Inconel 718 enriched in titanium, niobium, aluminum, and manganese oxides and in an oxycarbide of chromium, but leaves the Hastelloy passivated with an oxide of chromium that is thicker than the Inconel oxide. Other impurity levels did not substantially change.
3. The alkaline KMnO_4 plus HCl acid "oxide removal" for 50 min removes from the Inconel and Hastelloy

surfaces the oxides that result from the sealing operation, but reoxidizes the Inconel 718 surface with an even thicker oxide. Also following this treatment, the surface impurity levels of sulfur, chlorine, sodium, potassium, and calcium are significantly increased on both the Inconel and Hastelloy surfaces. Contact of a sealed Inconel specimen with the "oxide removal" solution for only 2.5 min leaves a thinner oxide.

4. (a) The argon plasma treatment removes the alkaline KMnO_4 -produced oxide from Inconel 718, (b) the O_2 plasma treatment enriches both superalloy surfaces with NiO , (c) both argon and oxygen plasma treatments reduce the overall surface contamination, i.e., chlorine, carbon, and sodium, and (d) electropolishing produces a very thin surface oxide of NiO .

This report clearly shows that metal surface treatments affect nickel-based superalloys differently and, thus, demonstrates the importance of monitoring changes in surface stoichiometry following various metal treatments with Auger electron spectroscopy and depth Auger profiling.

As a result of this study, processing changes in the cleaning of the glass-ceramic headers have been recommended.

It is important to note that different surface stoichiometries resulting from the various metal treatments could affect glass-ceramic to metal bond strengths.

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Appendix

TRITON[®] N-101

TRITON N 101 is a biodegradable liquid anhydrous nonionic surfactant. It is a water soluble nonyl-phenoxy polyethoxy ethanol containing 9-10 moles of ethylene oxide and is supplied as 100 percent active material. TRITON N 101 is useful as an emulsifier, wetting agent, and detergent.

APPLICATIONS

TRITON N 101 is useful in many applications requiring good detergency and wetting. It can be used to improve the detergent and wetting properties of formulations for laundry applications, metal cleaning and specialty items designed for home and industrial use.

TRITON N 101 offers effective hard-surface detergency and is recommended as a base ingredient in floor cleaners, detergent-sanitizers, liquid hand dishwashing detergents, and metal cleaners.

TRITON N 101 can be added to powdered preparations to reduce dustiness at levels of 0.5 percent to 1.0 percent. Various powdered formulations can be prepared that contain up to 10 percent TRITON N 101, but still remain free-flowing.

TRITON N-101 is an excellent wetting agent and is useful in applications demanding rapid wetting action. This characteristic, in conjunction with good detergency on fabrics, makes the product well suited for specialized applications such as hand washing of delicate synthetic fabrics.

Formulation recommendations are available upon request.

PHYSICAL AND CHEMICAL PROPERTIES *(These do not constitute specifications)*

Appearance	Clear haze free liquid
Color	100 APHA (maximum)
Odor	Mild
Viscosity (Brookfield)	240 centipoises at 25°C
Pour Point	4°C (40°F)
Specific Gravity	1.046
Density, lb/gal	8.7
pH (5% aqueous solution)	5.0-7.0
Cloud Point (1% aqueous solution)	52-58°C (126-136°F)
Flash Point (TOC), °F	> 300

CS-408
(Supersedes CS-408 12/79)

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May 1981

Product Data

SPAN[®] 80

Description

Sorbitan monooleate NF

General Characteristics

Classification	Nonionic surfactant
Form @ 25°C	Yellow liquid
Specific gravity @ 25°C /25°C	Approx 1
Viscosity @ 25°C	Approx 900 cps
Flash point	Above 300°F
Fire point	Above 300°F
HLB number	4.3

Solubilities

- (a) Soluble in most mineral oils and vegetable oils, ethyl acetate and Cellosolve
- (b) Insoluble in water, acetone, propylene and ethylene glycols

Standard Specifications

Acid number	8 max
Saponification number	145 - 160
Hydroxyl number	190 - 215
Water, %	1.0 max

Conforms to NF Specifications for Sorbitan Monooleate

Safety

SPAN 80 can be considered a "relatively harmless" substance. It was neither a skin irritant nor sensitizer in human patch tests, and was determined to be "nonirritating" to rabbit eyes in animal testing.

No problems have been encountered to date in handling this product; however, reasonable precautions should be observed during its use. Additional testing is recommended when a product is mixed or blended with other compounds.

Soak up spills with an absorbent such as sand, earth, sawdust or synthetic absorbent, and shovel into waste container. Wash down spill area with hot water containing detergent. Dispose of waste material in accordance with local pollution guidelines.

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