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Scanning AES and XPS analysis of a thin Au emissivity barrier on Ni alloy

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Scanning Auger electron spectroscopy and x-ray photoelectron spectroscopy were used to analyze discolored gold plating on nickel alloys. Gold plated nickel alloy sheets have been used as a thermal shield inside nacelle housings for various jet engines. The thin gold film is applied to serve as a low emissivity coating to reflect thermal radiation. Inconel 625 sheet was gold plated and exposed to 590°C in air for 924 hours to achieve an appropriate service use reference point. The visual appearance of the gold thin-film surface had noticeably dulled after this prolonged exposure. In some cases, several dark spots a few microns in size also appeared on the dulled gold surface. Our hypothesis was that nickel or some alloy constituent had diffused through the gold film and changed the color of the gold surface. X-ray photoelectron spectroscopy and Auger electron spectroscopy were used to differentiate the composition of the gold plated Inconel samples prior to thermal exposure and after the prolonged exposure. Scanning Auger micrographs showed that the composition of the dulled gold surface had changed due to the diffusion of nickel from the substrate alloy through the gold thin film. Nickel was absent at the surface of the unexposed samples while significant nickel concentrations were detected on the discolored gold surface and with the highest nickel levels detected in the dark spots on the gold surfaces. Auger depth profiles made on the exposed gold film verified that a discrete gold layer remained on top of the Inconel with a broad Ni-Cr-Au zone beneath this gold layer.

1. Introduction

Aerospace materials used in high temperature environments generally require thermal insulation and emissivity barriers to reduce the amount of absorbed thermal radiation. Thin gold films have been used to provide such low emissivity coatings on stainless steel, titanium and nickel alloys [1]. This study was carried out to investigate the use of a previously untried nickel alloy covered with the standard gold coating as a thermal barrier. Auger electron Spectroscopy (AES) has been used to examine various diffusion problems. Numerous papers studying diffusion with Auger analysis and other techniques are found in the literature [2–6]. While Auger electron spectroscopy and x-ray photoelectron spectroscopy (XPS) are often used in surface studies, little of the literature deals with aerospace materials and applications. Aerospace manufacturing often uses empirical environmental tests on candidate materials to examine a particular material's usefulness in a specific service condition. Aerospace service conditions are often harsh and materials may degrade after an extended service life. Nacelle housings and other jet engine components are regularly subjected to high temperatures, often with exposure to corrosive liquids and gases. Nickel alloys work well in these kinds of environments, but gold is much more resistant to corrosion from hydraulic fluids and fuels. High temperature components requiring corrosion resistance have an increased life span when

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gold coated [7]. By eliminating nickel or nickel oxide at the surface, the chances of stress corrosion cracking is greatly reduced. The lower emissivity value of the gold thin film reduces the amount of thermal radiation absorbed and increases the materials in service flight time. The durability and strength of the nickel alloys are leveraged and reduced labor costs are realized in the process.

2. Experimental

2.1. Samples

Inconel 625 plates 1mm thick were cut into 100×150 mm panels and coated with a thin gold film per the Boeing Company specification BMS 10-82B [8]. Inconel 625 is a high temperature nickel alloy consisting mostly of Ni, Fe, Cr, with trace amounts of Co, Mn, Cu, W, and V [9]. One group of test panels was set aside as control specimens while a second group of test panels was heated in an industrial oven to simulate the exposure of an engine nacelle. The gold-coated Inconel test coupons were subjected to a constant high-temperature exposure at 590°C in air. Periodic visual inspections were made each week on the samples. A visual check performed at 924 hours revealed a distinct color change visible in the gold coating. Closer inspection revealed small dark dots appearing on the gold surface. XPS and AES survey scans were taken on the control specimens and on the discolored gold film and dark spotted regions of the heat exposed samples. A depth profile was also made on the control sample to confirm the thickness of the gold film.

2.2. XPS

Surface analysis instrumentation and theory have been well described in numerous reviews [10–12]. An M-Probe Spectrometer made by Surface Science Instruments was used to generate the XPS data. Monochromatic AlKα (1486.6 eV) x-rays produce photoelectrons that were measured in a hemispherical energy analyzer at various pass energies. A pass energy of 150 eV was used to acquire wide spectra for determination of elemental surface composition. A constant take-off angle of 55° was maintained between the sample surface and the analyzer confining the analysis depth to the top ten to twenty atom layers or roughly 2.5–5 nm of the sample surface. The analysis area was an elliptical spot of approximately 1.7 mm $\times$ 0.4 mm. The XPS analyses were conducted under a high vacuum environment with pressures lower than 1×10^{-8} torr.

2.3. AES

A modified PHI 600 Scanning Auger Microprobe was used to probe the specimens. The instrument's primary electron beam was run at 5–10 kV, producing Auger electrons from the surface of the specimens that were measured with a cylindrical mirror analyzer. Like XPS, the analysis depth is very shallow, on the order of 5–10 nm. The system is also equipped with a Duoplasmatron 06-650 Microbeam Ion Gun that was used for depth profiling by sputter etching using Ar^+ ions. The sputter rate was determined to be 48 nm/min for a silicon dioxide calibration wafer. The data acquisition and mapping system was modified with an RBD Enterprises' Scanning Pentium-based computer module with broad bandwidth deflection electronics. This improved the electron beam stability of the system and also provided a Windows-based acquisition and data processing environment. All electron gun functions are handled through a RBD 110 Scan Interface with Augerscan and Augermap software loaded on the computer. A digital video system facilitates direct acquisition and storage of reference images eliminating the use of film and streamlines the documentation process [13].

3. Results and discussion

Wide scan XPS surveys were made on the control gold thin films and on the specimens exposed to the high temperature environment. In each of these spectra, a significant amount of C, N, and O was detected. These elements are attributed to contamination that is commonly found on as received industrial metal surfaces and are not investigated further in this study [14]. Three separate regions were targeted with five spectra ($n = 5$) taken within each region. The atomic compositional differences are shown in Table I. In the first column, the analysis of the gold thin film with no heat exposure is noticeably free of any Ni. The other trace metals are not considered. The origin of Bi, Pb, and Sn are not known, but likely are trace metals present in the plating process. The specific chemistry of the plating is proprietary and is not discussed here. The center column of Table I presents the analytical results on the dulled area showing a significant increase in Ni with a corresponding reduction of approximately 43% in Au concentration at the surface. This increase in Ni and Cr and the reduction in Au intensity is evidence that Ni and Cr have migrated from the substrate to the surface. These elements diffused through the gold over-layer, causing the gold film to lose some of its luster and thermal barrier effectiveness after the prolonged heat exposure. The XPS data from the dark spots, shown in the third column, reveal that there is a large increase in Ni and O and simultaneously an approximate 68% reduction in Au intensity. The level of O has increased by nearly 60%. These results indicate the Ni that diffused through the gold to the surface has oxidized in the furnace, turning it dark. The

TABLE I XPS elemental composition summary demonstrates the changes in gold thin film surface chemistry as a function of thermal exposure

Element	Bright gold no heat exposure Atomic %	Dull gold region 924 hours 590C Atomic %	Dark spots on gold 924 hours 590C Atomic %
Ni	0.0 ± 0.00	0.9 ± 0.46	6.4 ± 0.54
Cr	0.6 ± 0.04	2.6 ± 0.01	3.5 ± 0.25
O	28.7 ± 0.12	30.3 ± 0.96	44.9 ± 0.11
V	0.6 ± 0.04	0.5 ± 0.04	0.7 ± 0.09
Sn	0.1 ± 0.01	0.0 ± 0.00	0.2 ± 0.04
N	5.1 ± 0.02	6.5 ± 0.75	0.0 ± 0.00
Rh	1.1 ± 0.04	0.7 ± 0.01	0.4 ± 0.07
C	43.5 ± 0.42	46.9 ± 0.10	32.1 ± 1.28
Bi	1.3 ± 0.20	1.6 ± 0.12	2.5 ± 0.74
Pb	0.1 ± 0.06	0.0 ± 0.00	0.4 ± 0.09
Si	0.0 ± 0.00	0.0 ± 0.00	3.4 ± 0.51
Au	18.9 ± 0.32	10.8 ± 0.49	5.6 ± 0.55

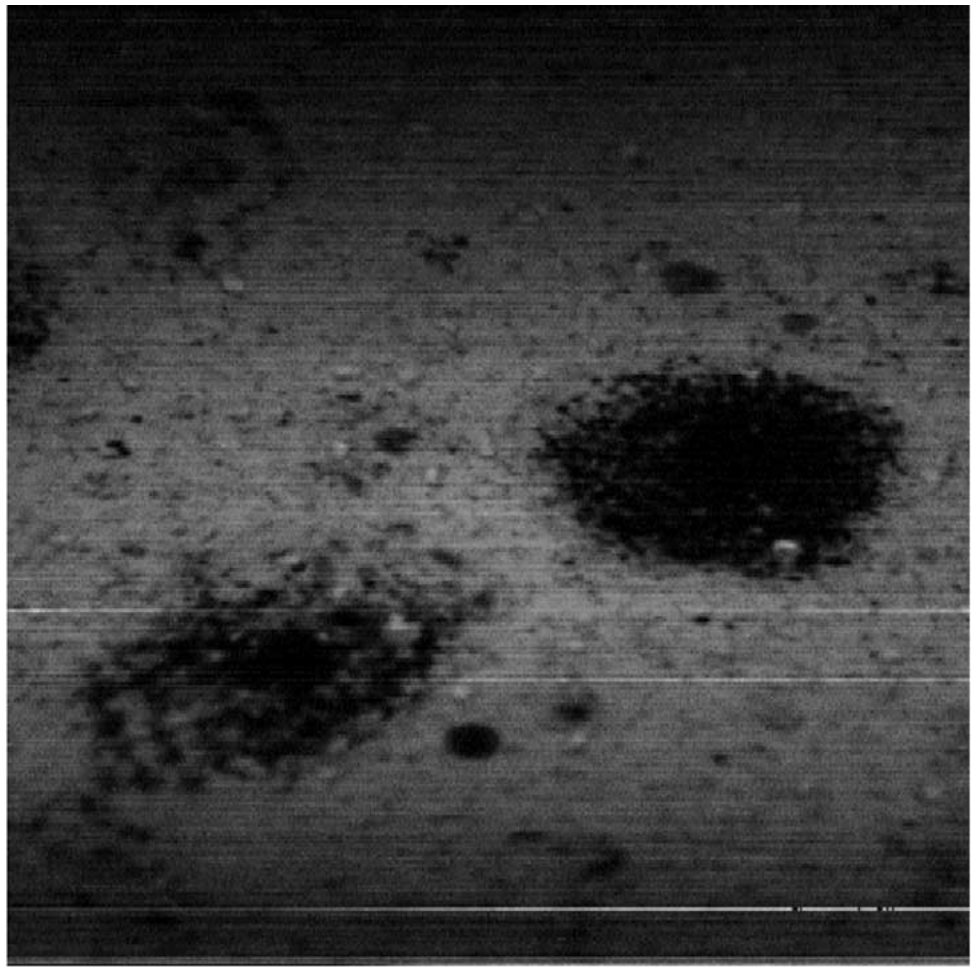

Figure 1 Scanned Auger gold map; 400 × 400 μm region from dulled gold surface including dark spots. Light areas correspond to Au.

Bi and Si intensities also increased and are likely trace metals in the gold film from the plating process that also move towards the surface upon heating. Although the small dark spots observed in the heated sample were often smaller than the beam size of the monochromatic x-ray spot, the table shows a clear difference in the Ni concentrations, increasing significantly when the majority of the photoelectron flux originated from the dark regions.

Auger maps of these regions further illustrate the case presented by the XPS data. The following three figures are Auger maps of 400 μm regions. Most noticeable are two roughly elliptical regions approximately 80 × 100 μm in size. The three maps are identical regions scanned over a section of the dulled gold thin film containing dark spots due to the prolonged heat exposure at 590°C. The light regions correspond to the highest concentration found for the scanned element while the darkest region in a map correspond to the lowest concentration for the same element. The scanned Auger map in Fig. 1 was generated from the intensity of the Au peak at 2024 eV. The features of these dark spots are accentuated with the surrounding light region where the Au concentrations are strongest. The dark spots are clearly due to some element other than Au. The map in Fig. 2 was generated from the intensity of the Ni peak at 848 eV. In this case, the contrast is reversed from the features in the gold map. A comparison readily shows that the Au is strongest where the Ni is weakest and the Ni is strongest where the Au is weakest. The map in Fig. 3 was generated from the intensity of the O peak at 503 eV. This map confirms a stronger O presence in the features corresponding to the Ni rich zones. These images combined with the data in Table I indicate that the dark spots on the surface of the gold film are oxidized nickel and chromium.

Auger point analyses conducted on specific features from these mapped zones quantify the results from the Auger maps. The survey spectrum in Fig. 4 shows the composition of the control sample, that is the gold film on the Inconel 625 prior to any heat exposure. The control surface is 60% Au and no Ni is detected. The regions labeled as 1 and 2 in Fig. 3 were also probed and compared with this control survey. Point 1, the region appearing dull gold after the 924 hour exposure at 590°C in air has a Ni atomic concentration of 1.6% (see Fig. 5). The surface is still mostly Au, ∼50%, a 16% decrease from the control surface. The normal adventitious carbon and trace elements found in the gold coating solution were also detected. Spectra from point 2, taken from the largest dark spot shows almost a 71% reduction in Au concentration from the control surface with large increases in Ni and O, corresponding to the Ni diffusing through the plating and oxidizing at the surface (see Fig. 6). The Auger data (Figs. 1–6) and the XPS data in Table I both show the same trend with heat treatment.

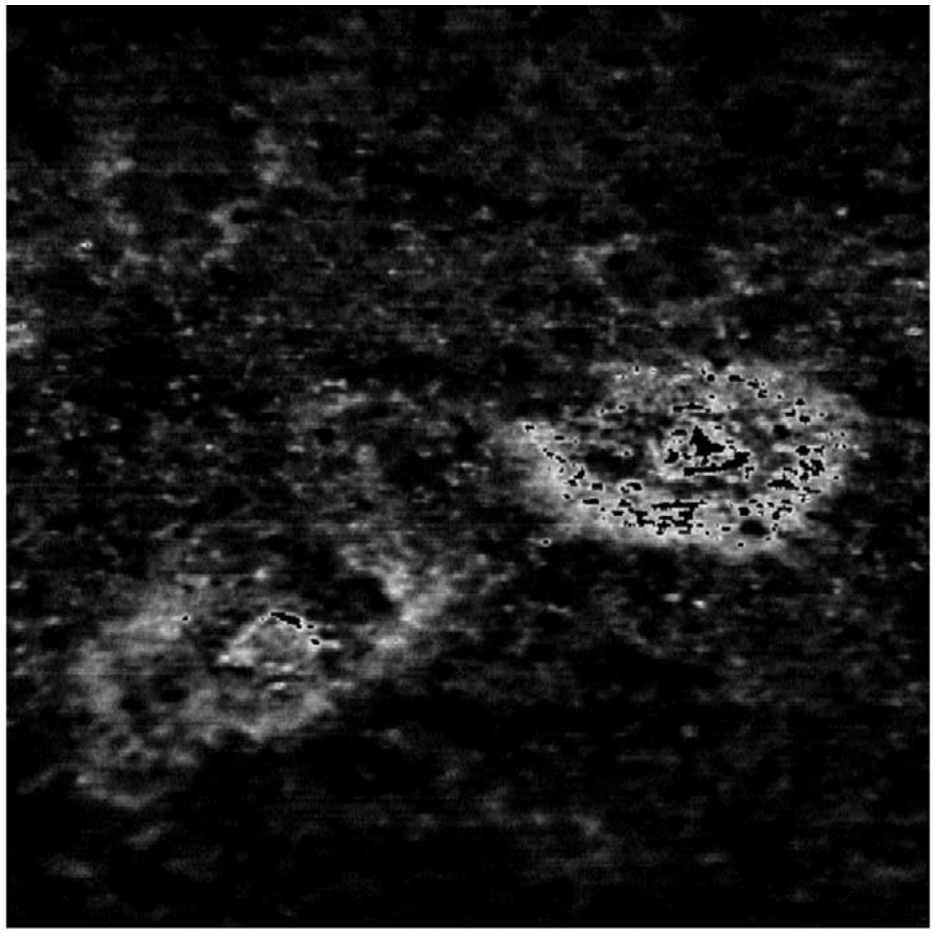

Figure 2 Scanned Auger Nickel Map; 400 × 400 μm region from dulled gold surface including dark spots. Ni concentrated in light regions.

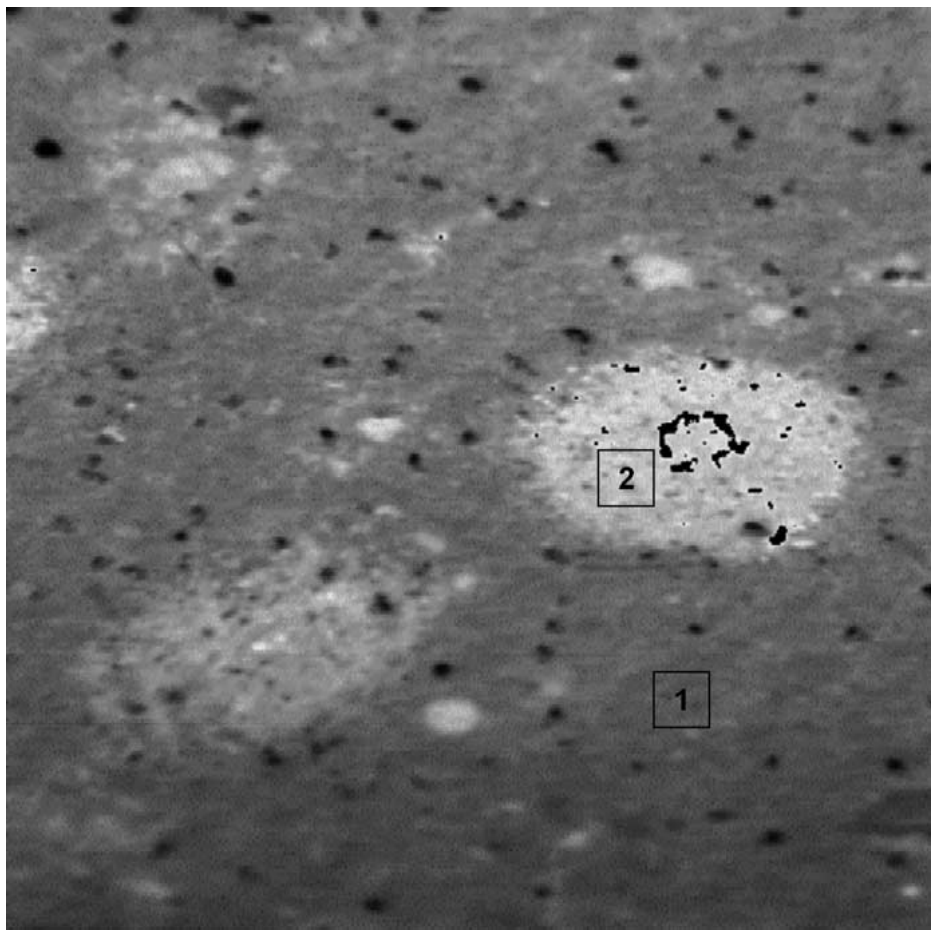

Figure 3 Scanned Auger Oxygen Map; 400 × 400 μm region from dulled gold surface including dark spots. Surface oxide concentrations are highest in regions corresponding to the dark spots.

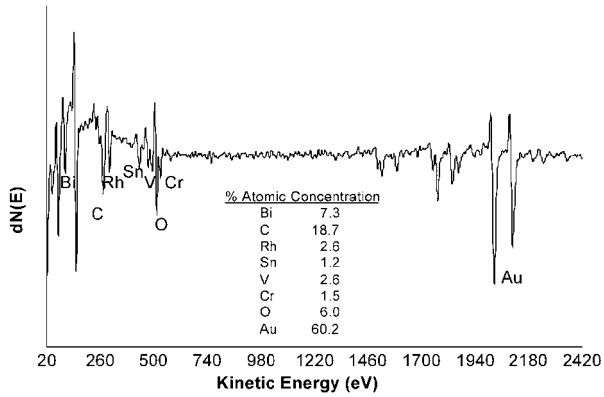

Figure 4 Auger wide survey spectrum of Inconel 625 with Au thin film as received, no thermal exposure; Analysis taken from surface area with bright gold appearance.

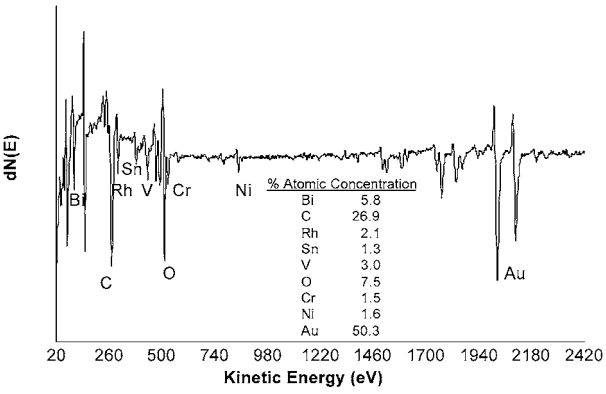

Figure 5 Auger wide survey spectrum of Inconel 625 with Au thin film; Analysis taken from surface area appearing as dull gold after 924 hours of heat exposure at 590°C.

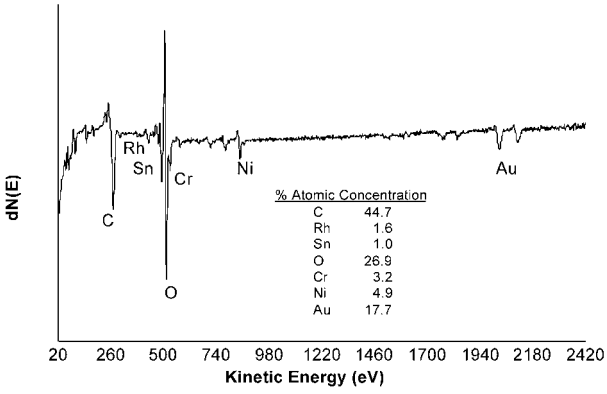

Figure 6 Auger wide survey spectrum of Inconel 625 with Au thin film; Analysis taken from dark spots appearing through the dulled gold region after 924 hours of heat exposure at 590°C.

The subsurface concentrations of Au, Ni, Cr and O were determined from an Auger depth profile taken of the heat exposed specimen on a region (point 1) where the appearance was of the gold film was dulled, but without the dark spots. The depth profile, presented in Fig. 6, indicates that the gold film is etched away after approximately 0.5 μm. Previous work on polished metallurgical cross sections indicated that the gold film was at least 4 times as thick [15]. The shallow location of the Ni-Au and the Cr-Au interface is further evidence of the Ni and Cr diffusion through the Au plating.

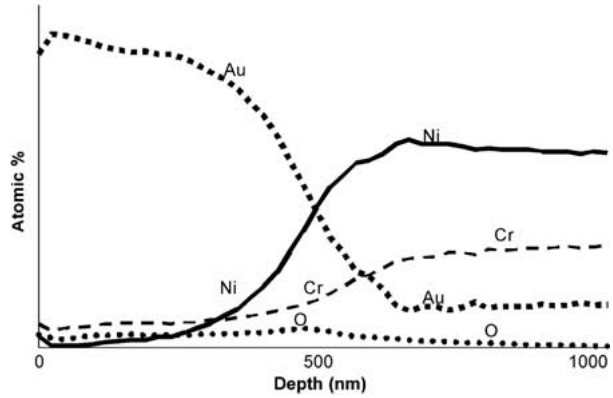

Figure 7 Auger depth profile of the dulled gold region after 924 hours of exposure at 590°C.

4. Conclusion

The original hypothesis, based on visual observations of the samples that Ni and other constituent elements had diffused through the thin gold film on the Inconel 625 substrate and oxidized was verified. Surface analysis made on the control and the heat exposed samples provided the evidence to support the case for diffusion. Ni, Cr and O increased in atomic concentration at the surface as a result of the heat exposure while the Au simultaneously decreased in concentration at the surface. These data points were duplicated with very good agreement. The complementary analysis using the more detailed and feature oriented Auger methods confirmed the XPS evidence and provided images to corroborate the spectral evidence. Aerospace materials destined for high-temperature applications may benefit from similar surface analysis experiments, which can speed up the materials and process specification cycle time.

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