Novel Insights into In-Service Oxidized Inconel 625 Engine Exhausts by a Multi-Technique Approach

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Ni-based superalloys are used as structural components in demanding high-temperature environments such as discs in jet engines and high performance engine exhausts. In these there is still a need to understand how the alloys behave under reactive conditions, as fundamental changes to the surface/near-surface alloy composition and microstructure can limit the component lifetime. This information would allow designers to produce lighter components operating at higher temperatures, improving performance and fuel efficiency. However, these are highly complex engineering alloys, and attempting to analyze them after exposure to aggressive oxidation conditions further complicates the task, particularly when looking at "in-service" materials rather than simulated conditions.

In this work, we have explored the oxidation behavior on an Inconel 625 alloy as used in a high-performance engine exhaust manifold. The extracted section from this was exposed to engine exhaust gases and particulates in a highly-dynamic transient cycle during an auto-racing environment. The total time period of exposure was 31hours, with temperatures ranging over approximately 650-1000°C at a pressure of ~5bar (7bar peak), after which the component failed through a bending mode. This is an extremely challenging system to study from a materials science perspective. To make progress multi-technique approaches are essential, combining information across different length-scales to build up a full picture. We demonstrate the power of this methodology using a combination of Focussed-Ion Beam (3D) slicing, SEM, X-Ray Photoelectron Spectroscopy (XPS) and Atom Probe Tomography (APT).

We firstly analyzed a stock sample of as-received (heat treated at 1040°C) Inconel 625. Table 1 shows the numerical data from the alloy manufacturer (Special Metals) using X-ray Fluorescence and from an electropolished sample analyzed by APT. The agreement between compositions is very good. XPS was also used to examine the as-received material, before turning to the surface and near-surface chemistry of the oxidized sample shown mounted in Fig. 1a). The composition of the outer surface is mainly C and O, however using ion-bombarding to dig below any surface contamination (a few tens of nanometers), C (40at.%) and O (34at.%) species are again detected along with unexpected Cu (7at.%), Zn (2at.%) and Na (6at.%), Fig. 2b). This suggests upstream contamination, possibly from fuel additives/lubricants.

FIB sectioning reveals further oxidation-induced features, Fig. 2a). At the top surface, we see a corrugated but complete oxide layer, ~1-2μm thick. Below this a number of small dark precipitates are concentrated along grain boundaries to a depth of ~5μm. At this same depth we also observe a number of large voids, 3μm in diameter with the centers located at grain boundary intersections. The prevalence of these may have played a role in the component failure. Deeper down a zone of ~10μm is precipitate-free, followed by a final layer of larger precipitates again concentrated along grain boundaries. The chemistry of the oxide/precipitates is currently under investigation, but based on a comparable SEM/EDX study on furnace oxidized Inconel [1] the oxide is likely Cr_2O_3, the dark precipitates Al_2O_3 and the deepest precipitates M_6C carbides (M=Ni, Mo). What is striking however is that in this previous work the alloy was exposed for 1000hours, but after only 30hours in this study we see similar features.

Preparing an APT sample from this is challenging, and requires sampling from multiple locations avoiding any voids to explore the full microstructure. Nevertheless we have recently carried out the first FIB-liftout experiment on this type of "in-service" component, extracting a sample ~1μm below the surface. The resulting atom maps are shown in Figure 2b) and c). In b) the major constituents of the alloy are shown, along with an oxygen iso-concentration surface clearly shows the formation of oxide bands spaced approximately 10nm apart. In c) minor species of C and also Na as identified in the XPS are shown accumulating at the lower iso-surface, while Cu and Zn (not shown) were also confirmed throughout the volume.

at.%	Ni	Cr	Fe	Mo	Nb	Co	Mn	Al	Ti	Si
XRF	60.8	25.1	4.8	5.5	2.3	0.2	0.06	0.6	0.5	0.2
APT	61.0	24.3	4.6	5.8	2.7	0.1	0.06	0.6	0.5	0.3

Table 1. Compositions of as-received Inconel 625 determined by supplier and by APT.
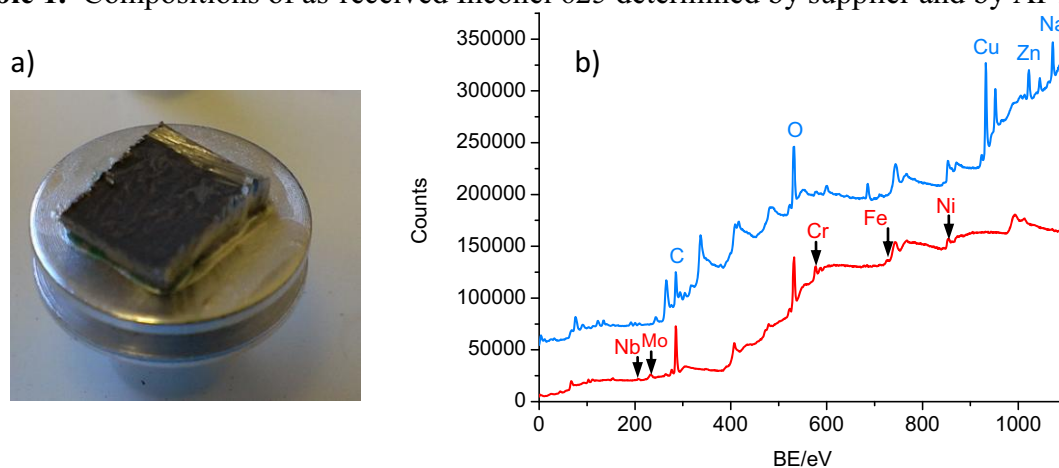
Figure 1. a) Extracted sample from oxidized Inconel 625, b) XPS spectra from near-surface (blue) of sample shown in a), and of as-received alloy (red), selected elements shown.
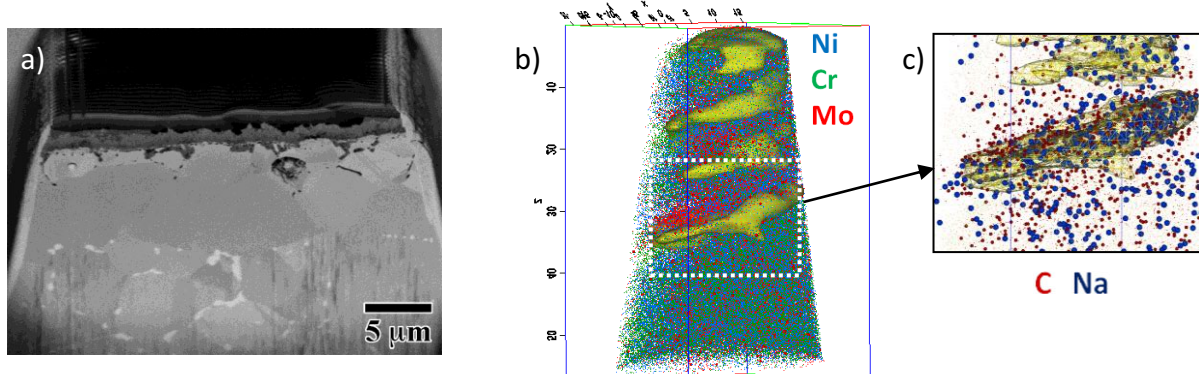
Figure 2. a) SEM image of oxidized Inconel 625 during FIB slicing, revealing oxide cap, G.B. precipitates, precipitate-free zone and void at G.B. intersection. b) APT reconstruction from oxidized alloy, extracted ~1μm from surface showing main species and oxide band (oxygen iso-surfaces set at 21atoms/nm^3). c) Magnification of lower oxygen iso-surface, showing C and Na segregation to oxide.

[1] A. Chyrkin et al., Oxid Met 74 (2011) 143