Technical Document

FLUOROCARBON CLEANING PROCESS

THE ULTIMATE CLEANING PRETREATMENT FOR SUPERALLOY REPAIR
1. THE NEED FOR HALIDE CLEANING

All aviation gas turbine engines require regular overhaul, to ensure continued safe operation. During engine overhaul decisions must be made, whether to replace deteriorated individual parts and assemblies with new components, or to repair them. The ultimate decision depends on both technical and commercial criteria. That is, is there a technically sound repair available and if so is it economically favourable, compared with the cost of a new replacement? Sometimes component supply problems may override purely economic criteria.

The complexity of many modern turbine section components, both in design and material, makes them very expensive and therefore economically prime candidates for repair. This is particularly true for many hot section airfoils.

Service deterioration of this type of component is mainly of thermal origin, which manifests itself as cracking and/or loss of material, caused by a combination of the following mechanisms: sulphidation, oxidation, hot corrosion, foreign object damage and thermal fatigue. Internal damage or deterioration by creep and micro-structural degradation may also occur.

While the extent and recoverability of internal structural deterioration incurred must always be taken into account in assessing the viability of any repair, halide cleaning is particularly relevant to the rectification of external damage, through the healing of cracks and restoration of component shape and form.

Such rectification can only be achieved by the local addition of new material. This requires the application of a fusion process and may be accomplished by direct welding and/or brazing, or by inserting a patch which itself requires welding or brazing.

However even before addressing the problems of choosing or developing suitable weld or braze filler alloys and application techniques, we have major difficulties to resolve:

1) Many of the alloys encountered are virtually unweldable and are impossible to braze by conventional means.

2) Cracks cannot be cleaned of oxides and other contaminants to allow braze infill or defect free welds.

It is evident therefore that some sort of enabling process is required to prepare and condition damaged engine run superalloy components, prior to attempting braze or weld repairs.

A necessary requirement of such a process is the ability to completely remove all traces of surface oxides and entrapped oxide in deep tight cracks. While many metal oxides may be reduced by hydrogen or vacuum treatment at high temperature, stable oxides such as the oxides of aluminium and titanium cannot be reduced in this manner. These elements are present in significant quantities in the gamma prime hardened nickel-based superalloys and form complex stable oxides, which cannot be removed by such means.

Fortunately however these oxides can be removed by treatment in a halide cleaning process, such as the Fluorocarbon Cleaning Process (FCP). In addition the FCP depletes surfaces in a controlled manner, even deep tight crack surfaces, of the strong oxide formers like aluminium and titanium, thus altering the surface chemistry and actively promoting braze wetting and crack infill of hitherto unbrazeable superalloys. The benefits of fluorocarbon cleaning are not confined to the braze repair of gamma prime nickel-based superalloys. Cobalt-based superalloys, for instance, do not contain aluminium or titanium and may be cleaned and brazed by conventional hydrogen or vacuum techniques. However in practice, difficulty is experienced in removing all traces of oxide and contaminants from engine induced cracks by such treatments, while FCP treatment results in 100% crack cleaning.
The intense crack cleaning and surface chemistry modification achieved by the FCP, has been found helpful in welding some difficult to weld superalloys. In addition to the above the FCP user will soon find many other applications for his process.

Taking all the foregoing into account it is apparent that any aero-engine overhaul or repair facility engaging in serious repair of turbine components, will find an effective halide cleaning system essential to its operation. Figures 1 and 2 show nozzle guide vanes before and after fluorocarbon cleaning.

2. THE HALIDE CLEANING PROCESSES

- Historical data.

The halide cleaning technique is not a new process. On the contrary, it has been known to the industry for many years.

As long ago as 1951 three patents were filed at the U.S. Patent Office on behalf of Edson and Newell involving a process of fluxing and joining metal parts. In these patents the inventors claimed amongst other points -The process of joining metals by solder, in which a stable inert gaseous atmosphere has as its active component a fluorine-containing compound, which is reactive with the oxides of the metals... etc. (1,2). In February, 1952 Moore and Edson filed another patent, regarding a process of joining metals, in which they claimed a stable non-oxidizing atmosphere containing hydrogen fluoride (3).

In November, 1972 at the first International Brazing and Soldering Conference in London Genieys presented a paper called - Brazing in reducing fluoride containing atmospheres (4).

In January, 1973 a patent was filed at the U.S. Patent Office on behalf of Galmiche and Co. which described a method for the manufacture of a composite refractory metallic element with porous coating. The patent describes the application of an abradable porous metallic coating, on a casing of nickel-based alloy. The coating is bonded by brazing to the casing, by carrying out the brazing in a hydrogen fluoride atmosphere (5).

At the American Welding Society Meeting in Philadelphia in April, 1977 a paper was presented by Parmentier and Calmas, called - Brazing stainless steel in a stable reducing atmosphere retort in an air atmosphere furnace. The apparatus used to accomplish the cleaning techniques is simple heat treatment equipment, such as a hydrogen atmosphere retort in an air atmosphere furnace. The process technique using the mixture of chromium and ammonium fluoride was given the nickname 'Big Burp', because of environmental and safety problems experienced due to rapid evolution of ammonium fluoride gas at 260° and the subsequent overloading of the exhaust system. The technique using chromium fluoride produces less gas evolution and is known as the 'Little Burp' technique (12).

Chromium fluoride processes are considered somewhat dated. The presence of moisture decreases the reducing atmosphere, causing only a part of the complex and stable oxides to convert into their volatile fluorides, resulting in less clean cracks. In addition the process depletes the surface only slightly which is not conductive to good brazing.

By 1985 Ti-Coating Inc. Mt Clemens, Michigan had developed and manufactured a halide cleaning system which uses hydrogen fluoride (HF-gas). The Ti-Coating equipment concept introduced precisely metered hydrogen fluoride and hydrogen gas into the reactor chamber (12).

The Chromium Fluoride Systems (CrF₂, NH₄F + Cr)

Genieys explains in his paper - Brazing in fluorides containing atmosphere - that the fundamental principle developed by Galmiche and Co. is the use of a fluorinated atmosphere by the equilibrium reduction of metal fluorides, mostly chromium fluorides. Chromium fluoride (CrF₂) and hydrogen gas (H₂) will form hydrogen fluoride (HF). Genieys has used straight chromium fluoride, prepared in a separate operation or from a mixture of chromium powder and ammonium fluoride (4).

Keller and Resor use chromium fluoride which, when heated with hydrogen gas reacts to produce hydrogen fluoride (HF), the source of the gaseous active fluoride-ion (6). The cleaning step relies upon the subsequent chemical reactions, in order to form a gaseous atmosphere capable of fluoride-ion cleaning. Similar reactions take place in the Genieys and Galmiche processes (4,5).

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The Mixed Gas or H₂/HF Systems

In 1985 Ti-Coating Inc. introduced a halide cleaning system using hydrogen fluoride (HF). Chemically the Hydrogen Fluoride Cleaning Process is identical to the Chromium Fluoride Process, but it has one significant difference. Instead of obtaining HF-gas through secondary reactions, a small quantity of hydrogen fluoride (HF-gas) is introduced directly into the reactor system, through a precision electronic gas mass flow-meter (12). The mixed gas process converts the stable oxides into their fluorides by reaction with hydrogen fluoride. The hydrogen fluoride will also deplete the surface layer.

\[
\text{Al}_2\text{O}_3 + 6\text{HF} \rightarrow 2\text{AlF}_3 + 3\text{H}_2\text{O} \\
2\text{Al} + 6\text{HF} \rightarrow 2\text{AlF}_3 + 3\text{H}_2
\]

Here aluminium is used as an example but similar reaction occurs with titanium and chromium. The only solid reaction product is CrF₃ which is converted to solid chromium according to:

\[
2\text{CrF}_3 (\text{solid}) + 3\text{H}_2 \rightarrow 2\text{Cr} (\text{solid}) + 4\text{HF}
\]

Using pure hydrogen fluoride (HF) in a mixed gas system seems to be a reliable process. However, experience indicates that handling hydrogen fluoride gas is difficult and requires special safety precautions. In general parameters need to be tailored to avoid intergranular attack (IGA) (12). Each superalloy has its own parameters and cycles. Using hydrogen fluoride to clean cracks can create a situation where IGA occurs. As mentioned earlier the mixed gas process converts the stable oxides into their conjugate fluorides, according to the following reaction with hydrogen fluoride:

\[
\text{Al}_2\text{O}_3 + 6\text{HF} \rightarrow 2\text{AlF}_3 + 3\text{H}_2\text{O}
\]

Thus, water is produced each time the hydrogen fluoride converts an oxide to its fluoride. Moreover hydrogen fluoride (HF-gas), like its sister halogen counterparts is notoriously hygroscopic. Hydrogen fluoride gas, as is currently commercially available, contains a significant amount of water present as impurity. Hydrogen fluoride collects the most minute amount of water from the most innocuous sources. Hydrogen fluoride containing small amounts of water is ferociously corrosive. It creates a corrosion cell on the component between the grain boundaries and the matrix of the material, with the HF/water mixture as an electrolyte. Due to their composition, the grain boundaries are less stable than the matrix. The grain boundaries will become the anode in the corrosion cell and constituents will go into solution. The result of these phenomena is called intergranular attack (IGA).

The Fluorocarbon Cleaning System

J. Chasteen uses the thermal decomposition of polytetrafluoro-ethylene (PTFE or Teflon) as the source of elemental fluorine. The method is described as follows: The parts are placed on racks in a well sealed retort, containing inlet- and outlet ports. The Teflon is located upstream of the parts and heated with the parts through the Teflon decomposition temperature range, while introducing pure hydrogen through the inlet.

Hydrogen is a reactant but also acts as a carrier to exhaust the reaction products via the exhaust port through a scrubber, which removes all traces of HF-gas (7). The Fluorocarbon Cleaning Process occurs in three stages (9).

STAGE 1. Low temperature/Reduction of oxides

At this stage the Teflon is pyrolized in order to release the monomer, which in turn converts the stable oxides on the surface and in the cracks into their fluorides

\[
(\text{C}_2\text{F}_4)_n \text{solid} \quad \Rightarrow \quad n\text{C}_2\text{F}_4 \quad \text{(gaseous)} \\
\text{PTFE (Teflon)} \quad \text{(monomer)}
\]

\[
3\text{C}_2\text{F}_4 + 2\text{Al}_2\text{O}_3 \rightarrow 4\text{AlF}_3 \uparrow + 6\text{CO} \uparrow
\]

Here aluminium is used as an example but similar reaction occurs with titanium and chromium oxides. Only the formed chromium fluoride (CrF₃) is solid.

STAGE 2. Intermediate temperature/Depletion

At stage 2 the pyrolysis of Teflon is completed and the continued flow of hydrogen causes the atmosphere to become predominantly hydrogen fluoride as an active ingredient, according to:

\[
\text{C}_2\text{F}_4 + 6\text{H}_2 \rightarrow 4\text{HF} + 2\text{CH}_4
\]

monomer

This atmosphere reacts with aluminium and titanium on the surface of the alloy, where both elements are removed through the formation of their volatile fluorides. The resultant concentration gradient causes diffusion of both constituents from within the alloy to the surface.

\[
2\text{Al} + 6\text{HF} \rightarrow 2\text{AlF}_3 \uparrow + 3\text{H}_2 \uparrow
\]

Stage 2 accomplishes the depletion of a surface layer (10 µ to 20 µ) of aluminium and titanium, so that their oxides will not reform upon exposure to the air during brazing in a vacuum furnace. On completion of stage 2, one is left with a layer of cleaned depleted superalloy on the surface and on top of that, a thin layer of solid chromium fluoride.

STAGE 3. High temperature/Reduction

Stage 3 is entered when the atmosphere becomes predominantly hydrogen gas. At this time the solid chromium fluoride on the surface is converted to chromium according to:

\[
2\text{CrF}_3 (\text{solid}) + 3\text{H}_2 \rightarrow 2\text{Cr} (\text{solid}) + 4\text{HF} \uparrow
\]

Cleaning is then complete. At this point all surfaces to a depth of 10 µ to 20 µ are essentially the parent alloy less aluminium and titanium, but slightly enriched with chromium. A vacuum brightening is recommended to eliminate the finely divided chromium that remains on the surface. This elimination will ensure good braze flow on all points of the surface. Figure 3 shows a schematic of the FCP cycle and Figure 4 the measured Al and Ti depletion by scanning electronic microscope.
The exhaust gases from the retort run through a scrubber placed in the lid of the retort, filled with a sodium hydroxide solution. The following reaction takes place in the scrubber.

\[
\text{NAOH (solution)} + (\text{H}_2, \text{OH}, \text{HF}) \text{ gases} \\
\text{NAF (solution)} + \text{H}_2\text{O} + (\text{H}_2, \text{OH}) \text{ gases}
\]

The effluent gases can be easily controlled.

As mentioned in stage 1 the FCP converts most of the stable oxides into their conjugate fluorides, but the byproduct is carbon monoxide (CO) instead of contaminating water (H\text{2}O). The byproduct is CO because the formed methane (CH\text{4}) will react with water (H\text{2}O) to form CO.

\[
\text{CH}_4 + \text{H}_2\text{O} \Rightarrow \text{CO} + 3\text{H}_2
\]

Consequently intergranular attack (IGA) does not occur. Because most of the cleaning (removing stable and complex oxides) occurs in stage 1, the amount of hydrogen gas in stage 2 will determine the depletion depth. The nature of the process and the situation of the equilibria during each stage, allows the user to clean all known nickel-based superalloys using one set of parameters (one cycle). Figure 5 shows a crack in MAR-M200 + Hf material cleaned by FCP.

The Fluorocarbon Cleaning Process was invented and developed at the University of Dayton Ohio Research Institute by Dr. Jack Chasteen. It was applied industrially for the first time at ELBAR B.V. (The Netherlands) one of the Interturbine Companies (1981). Interturbine’s Holding Company (Indivers, NL) was the first licensee of the FCP in 1980. The process was installed later at Interturbine Holland (1985) as the enabling step for their wide-gap brazing (FAB). In 1986 Rolls Royce Plc. selected the FCP from a number of options and installed the Fluorocarbon Cleaning Process at East Kilbride (Scotland). Because the increased commercial interest had taken the process beyond the scope of the University of Dayton’s remit of research and development, agreement was reached with Rolls Royce Plc. and the Interturbine Group of Companies to create a joint-venture company which would develop and market the FCP commercially.

Dayton Process B.V. offers to the industry the Fluorocarbon Cleaning Process as a turnkey project, including equipment (Dayton Cleaner), commissioning, training and know-how. Dayton Process B.V., a joint venture of Rolls Royce Plc. and Interturbine has its office in Lomm (NL). Figure 6 shows a sketch of FCP Dayton Cleaner.
3. THE APPLICATION IN PRACTICE OF THE FLUOROCARBON CLEANING PROCESS.

Modern techniques for repairing gas turbine parts by brazing and welding, rely on the use of halide cleaning techniques such as the Fluorocarbon Cleaning Process. The FCP Process overcomes the two main barriers to successful brazing of engine run nickel-based and cobalt-based superalloys, by the removal of stable and complex surface oxides and conditioning of the component surface to promote braze wetting. For many years the University of Dayton, Rolls Royce Plc. and Interturbine have built up an extensive experience in using the FCP with positive results.

The following micrographs are from cracked engine run nozzle guide vanes, which had been FCP cleaned during normal production runs at Rolls Royce East Kilbride. The majority of the cracks were then brazed. Selected brazed and non-brazed cracks were sectioned and prepared for metallographic examination. Vanes used were both C-1023 (nickel-based) and Stellite 31 (cobalt-based) superalloys.

As previously stated the FCP is uniquely effective in solving both problems by treatment in stage 1 with Teflon gases, which convert the normally stable oxides to volatile or easily reducible fluorides. In addition in stage 2 the stable oxide forming elements such as aluminium and titanium in the alloy surface, are converted by hydrogen fluoride. Outward diffusion of these elements during the process results in a surface layer depletion of 10µ - 20µ, promoting braze wetting and free flow of the braze medium into tight cracks.

Stellite 31 is cobalt-based and contains no significant amount of the strong oxide formers aluminium and titanium. Strictly speaking surface oxides can be removed by vacuum or hydrogen reduction, leaving a bright brazeable surface. In practice however, tight engine induced thermal cracks are not cleaned sufficiently to allow effective infill and braze repair. The FCP of cracked S-31 components completely removes complex oxides from cracks and promotes 100% infill with braze medium. The degree of effectiveness of the FCP Process as an enabling process for brazing can be gauged from the figures 7 to 10.
4. CONCLUSIONS

An effective halide cleaning unit is an essential prerequisite to the successful braze repair of turbine components from modern aviation gas turbine engines. Of all the known cleaning processes and systems currently available, the Fluorocarbon Cleaning Process (FCP) is the most effective, most reliable and most attractive from health, safety and environmental aspects. The FCP is a unique ‘dry’ process which completely eliminates the problem of associated GA. It is the most effective process for the removal of surface and sub-cutaneous complex stable metal oxides from cracks, and free surfaces of nickel- and cobalt-based superalloy engine run components. Controlled surface depletion of strong oxide forming elements like aluminium and titanium, actively promotes good braze wetting and infill of even the most complex superalloys. This unique combination of cleaning and surface conditioning without attendant GA, makes the DAYTON FCP an ideal enabling process for the braze repair of today’s generation of engine run superalloy turbine components. See figures 11 to 14.

The micrographs illustrate the following features:

- The FCP is shown to be completely effective in the removal of surface oxides from tight engine induced cracks.
- The controlled depletion of the elements aluminium and titanium from the crack surface layers, actively promotes wetting and crack filling by the braze medium.
- The reduction and removal of sub-surface oxides, including long fingerlike intrusions typically found at the tip of service induced cracks can be completely achieved.
- The FCP of cobalt-based superalloy parts promotes infill with braze medium.
5. ACKNOWLEDGEMENT

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6. Users

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7. REFERENCES


Dayton Process B.V.

These documents published in 1990 are updated December 2002.

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DAYTON PROCESS B.V.

Dayton Process B.V. markets the technology relating to the Fluorocarbon Cleaning Process (FCP). Dayton Process B.V. achieves this purpose by offering know-how and services. Equipment for the Fluorocarbon Cleaning Process (FCP) is offered by Vac Aero International Inc.

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