THE USE OF COATINGS FOR HOT CORROSION AND EROSION PROTECTION IN TURBINE HOT SECTION COMPONENTS

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ABSTRACT

High pressure turbine components are subjected to a wide variety of thermal and mechanical loading during service. In addition, the components are exposed to a highly oxidizing atmosphere which may contain contaminants such as sulphates, chlorides and sulphuorous gases along with erosive media. So the variety of surface coatings and deposition processes available for the protection of blade and vane components in gas turbines are summarised in this study. Coating types range from simple diffusion aluminides to modified aluminides and a CoCrAlY overlayer. The recommendations for corrosion-resistant coatings (for low temperature and high temperature hot corrosion environments) are as follows: silicon aluminide and platinum-chromium aluminide for different gas turbine section superalloys substrates. Platinum metal additions are used to improve the properties of coatings on turbine components. Inorganic coatings based on ceramic films which contain aluminium or aluminium and silicon are very effective in engines and gas turbines. Diffusion, overlayer and thermal barrier coatings which are deposited on superalloys gas turbine components by pack cementation, plasma spraying processes and a number of chemical vapour deposition, physical vapour deposition processes (such as electron beam, sputtering, ion plating) are described. The principles underlying the development of protective coatings serve as a useful guide in the choice of coatings for other high temperature applications.

Key Words: Turbine gas section, Hot corrosion, Protective coatings, Thermal coating

SICAK TÜRBİN PARÇALARINDA SICAK KOROZYONDAN VE EROZYONDAN KORUNMA İÇİN KAPLAMALARIN KULLANIMI

ÖZET

Yüksek sıcaklık türbin malzemeleri sülfat ve klorürle birlikte aşındırıcı partiküllerin bulunduğu ortamda termal ve mekaniksel yüklenmeyle karşı karşıyadırlar. Bu incelemede gaz türbinlerinde kullanılan parçaların korunması için mevcut olan çeşitli kaplama ve biriktirme prosesleri özetlenmiştir. Basit diffüzyon kaplamadan modifiye alüminyum kaplamaya ve CoCrAlY tabakalı kaplamaya kadar birçok kaplama türü vardır. Koruyucu kaplamaların geliştirilmesinin altında yatan prensipler, diğer yüksek sıcaklık uygulamaları için kaplamaların geliştirilmesi ve seçiminde kullanışlı rehber olarak hizmet verir.

Anahtar Kelimeler : Gaz türbin ünitesi, Sıcak korozyon, Koruyucu kaplama, Termal kaplama

1. INTRODUCTION

Gas turbines are widely used in aero, marine and industrial sector as prime movers for oil and gas production. In mainly gas turbine, air enters the engine and is compressed by centrifugal or axial compressors: the temperature rises during the compression. Fuel is then injected and burnt: the

aim of this is to heat the compressed air to the entry temperature. The amount of fuel is always very much less than that of air, so the combustion gas is always very oxygen rich. The hot oxygen-rich gas then enters a row of stationary blades (the nozzle guide vanes) which turn the gas stream and may also accelerate it which provides the power to drive the turbine compressor. The gas then strikes a row of rotating blades fixed to the rim of a wheel which in turn is attached to the shaft. The combination of a stationary row of vanes and a rotating row of blades is called a stage and a turbine may have one or four stage. Blades which are present in the turbine have high temperature (Bhushn and Gupt, 1991; Sahm and Speidel, 1991; Radcliff, 1997). Figure 1 illustrates the temperature distribution on a blade (Stringer, 1997).
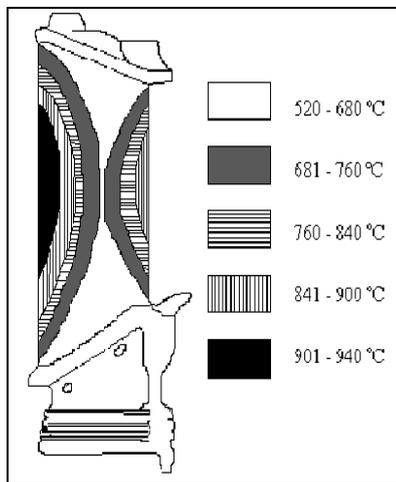
Hot section gas turbine components operate under complex and demanding combinations of stress and temperature in a high-velocity gas stream which may contain aggressive species arising from impurities in the fuel and entering air. Table 1 summarises the main contaminants likely to be found in working environments and the relative severities of surface-damage leading to failure for the three types of engine application (Saunders, 1986; Bhushn and Gupt, 1991; Sahm and Speidel, 1991). The principle degradation mechanisms for the hot gas path components are creep, fatigue and corrosion (Figure 2). These processes may act individually or in combination to limit the life of components. It can be seen from Figure 2 that the corrosion is high but the dominant degradation mechanism is creep for hot gas path components. Corrosion can be a specific problem in certain operating environment (Mevrel et all., 1986).

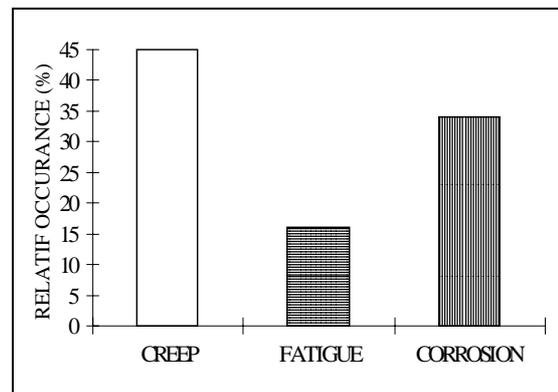Figure 1. Temperature distribution on surface of first stage blade (Stringer, 1997)

Figure 2. Failure mechanism for the hot gas path components (Radcliff, 1997).

Table 1. Contaminants In Gas Turbine Fuel and Air and Surface-Damage Mechanisms on Turbine Materials (Saunders, 1986; Sahm and Speidel, 1991).

Engine Applications	Contaminants	Oxidation	Hot Corrosion	Thermal Fatigue
Aero	Na ,Cl, S, Ca, (all low)	Severe	Moderate	Severe
Marine	Na, Cl, S, Mg (all high)	Moderate	Severe	Moderate
Industrial	Na, V, S, Pb, Cl	Moderate	Severe	Light

The pollutants entering with the inlet air and the fuel impurities affect the corrosion phenomena. Gas turbines engines in working environments are subjected to erosion and corrosion. The contaminant level depends on the turbine location. A marine environment contains high amounts of NaCl, while in industrial areas, a wide variety of pollution such as SO_2 etc., can occur depending on industrial plants. In desert regions, the contamination caused by the desert sand alkali salts, chlorides and other

species can reach high levels. In many instances, an air filtration is installed to reduce the corrosive and erosive impurities. The operating temperature is also important for the type of corrosion attack (Bürgel, 1986; Stephenson, 1989; Tabakoff and Metwally, 1992; Tabakoff et all., 1992).

The hot path components of a gas turbine operate in a highly oxidising environment and depend on the formation of compact oxygen layers to provide

protection. However when operating temperatures exceed design levels, oxidation can become a significant problem with turbine components. In aero engines, alloys forming protective alumina (Al_2O_3) scales are favoured for rotating components since this oxide is stable at very high temperatures. However, the breakdown of alumina scales can be increased by certain aggressive species arising from fuel and entering air impurities encountered in industrial engines. Therefore, alloys that form chromia (Cr_2O_3) scales which are more corrosion resistant are extensively used in industrial turbines for both rotating and static components. There is a limitation in the protection provided by chromia in that at high temperatures it oxidises further to form the gaseous chromium trioxide (CrO_3) (Goward, 1986).

Breakdown of the protective oxide layers by chemical interaction with certain aggressive species contained in the combustion environment can produce accelerated attack on the underlying metal. That is, the most important form of corrosion is the accelerated oxidation, which take place when the air or fuel is contaminated with certain impurities. Aggressive species are sodium (in the form of sodium sulphate), sulphur and vanadium (in the form of vanadium pentoxides). All these elements can be present as fuel impurities (Goward, 1986; Stringer, 1997).

Vanadium pentoxide can also produce extremely corrosive deposits. If the amount of vanadium present in turbine fuels is generally kept at low levels, then the associated corrosion is not a problem. On the other hand, vanadium-caused corrosion is generally controlled by the use of fuel additions. The most common additives contain magnesium and their action is to react with the vanadium oxides to form high-melting magnesium vanadate deposits. Vanadium-corrosion is also prevented by adding nickel into crude oil as an impurity (Goward, 1986).

Certain fuel impurities can also encourage hot corrosion, particularly marine turbine operation, either individually or in combination with known aggressive species such as sodium sulphate (Na_2SO_4). Two different forms of hot corrosion are distinguished: Namely type I and II. They occur over completely different temperature ranges. (850-950 ^{o}C and 650-750 ^{o}C respectively) (Czech, Eber and Schmitz, 1986; Goward, 1986; Ari-Gur, et all., 1991). Types I and II hot corrosion are known sulphidation and sulphation respectively. Although in sulphidation sulphur goes into the underlying metal to form internal sulphides, in sulphation

sulphur does not generally enter the alloy to form the internal attack. Turbines operating at high loads may experience type I hot corrosion on the blades and vanes, whereas low load operation cause type II corrosion. Both types of attack can also take place on the same surface as a result of thermal gradients. Zinc is another impurity that can be present in fuel as a result of corrosion of galvanised storage thanks and fuel-system components and can encourage sulphidation. In the sulphate form, zinc can produce low-melting eutectics with sodium sulphate which may increase type II corrosion. Other fuel impurities such as lead, chloride and calcium sulphate are known to increase hot corrosion (Steinmetz et all., 1986). In short, the hot gases are highly oxidizing and may contain contaminants and erosive media which react with turbine materials, so resulting in materials losses. This is the hot corrosion. Severe erosion of gas turbine components such as compressor blades can occur when sand and dust particles are ingested by gas turbine engine (Stephenson, 1989; Tabakoff and Metwally, 1992; Tbakaoff et all., 1992).

Materials used for the hot section components must have the appropriate mechanical and physical properties to suit the individual requirements for specific areas of the turbine. High temperature engineering alloys are based on the transition metals iron, nickel and cobalt, known nickel-base and cobalt-base superalloys, whose oxidation resistance can be improved by adding sufficient amounts of chromium, aluminium or silicon to form continuous external oxide (Cr_2O_3, Al_2O_3 and SiO_2) scales (Bürgel, 1986; Booth and Clarke, 1986; Eber et all., 1986; Steinmetz et all., 1986; Bhushn and Gupt, 1991; Sahm and Speidel, 1991; Tabakoff and Metwally, 1992; Stringer, 1997). These materials are subjected to high stress under complex thermal, mechanical, corrosive and erosive conditions (Figure 3).
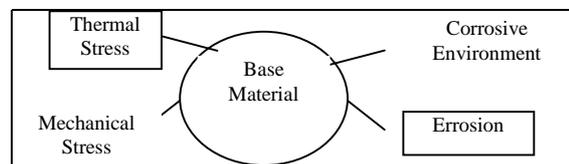

Figure 3. Main stresses on base material (Czech et all., 1986).

The combined effects of thermal and mechanical stresses and of the high temperature corrosion and erosion reduce the cross-section of component. So a reduction in the cross-section of a component can reduce the creep strength, and other mechanical properties, and it is obvious that an increase in

corrosiveness also reduces the properties (Bürgel, 1986; Czech et all., 1986; Tabakoff and Metwally, 1992; Radclıff, 1997; Stringer, 1997).

The nickel-base alloys used for hot section components in industrial turbines contain both chromium and aluminium. Nickel is a basic element of blade alloys , and forms stable, high-melting point intermetalic compounds with aluminium (NiAl, Ni_3Al). Aluminium and chromium are oxidised to form Al_2O_3 and Cr_2O_3 respectively which make it suitable for use up to at least 1200 ^{0}C. When chromium alloyed with nickel, cobalt, aluminium and silicon, it produces coatings resistance to sulphate corrosion. The aluminium is also present to stabilise the strengthening phase $\gamma(Ni_3(H,Ti)$. Furthermore internal oxidation of the aluminium in the alloy occurs at lower oxygen partial pressure than chromia. The internal alumina particles are useful in that they assist to form the protective surface layer of chromia. The most common nickel-base alloys used in industrial gas turbines are the cast alloy IN 738 2C, MAR-M421 for blades and IN 939 for vanes. However, the cobalt-base alloys such as FSX-414, X40 and X45 are preferred for vanes in most industrial turbines. The properties of the cobalt-base alloy depend on chromium, because it forms protective surface oxide layers (Goward, 1986). Therefore the materials able to withstand both types I and II hot corrosion are limited. The cobalt-base alloys are considered to have better resistance to type I hot corrosion than their nickel-base alloys, but they appear more sensitive to type II attack (Stringer, 1997). Although chromium is thought to improve the overall corrosion resistance of nickel-base alloy, the high chromium IN 939 with good type I resistance can show a poorer performance in type II conditions than lower chromium alloys such as IN 738. Additional corrosion resistance for hot section components is normally provided by the use of protective coatings (Booth and Clarke, 1986; Goward, 1986). By the mid-1950s high-temperature coatings were being applied to hot section gas turbine components. A wide range of coatings and coating processes are now available for protecting components in gas turbines under operating conditions.
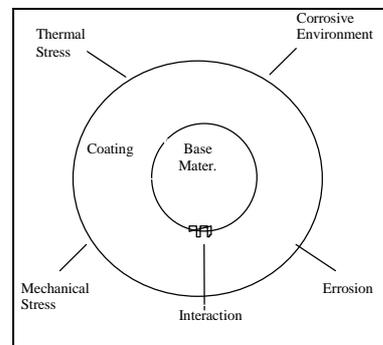
2. COATINGS ON THE GAS TURBINE COMPONENTS

Coatings for protecting hot section components from corrosion should be effective for as long as possible. The effectiveness of protective coating for a particular material under service conditions can therefore be assessed by all the parameters shown in Figure 4a. In addition to the uncoated base materials, the coating-substrate interaction is also taken into consideration in evaluating the performance of coated hot section components (Figure 4b).
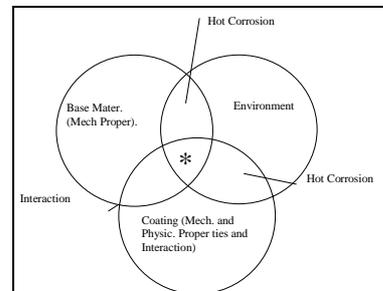
(a)

(b)

Figure 4. (a) Parameters affecting service conditions (*Effect of Environment on the mechanical properties of coated superalloys), (b) Factors determining effectiveness of coating (Czech et all., 1986)

Coating on the gas turbine components is common practice. In the selection of the appropriate coating it should be considered the varying running characterising of the turbine. It is known that turbine engines are exposed to different load and different temperature. In addition to chemical reaction, a coating is exposed to mechanical loading. The static load leading to creep deformation is not a major factor affecting coating degradation, but the thermal stresses which can exceed the coating strength lead to cracking. Also the erosive loadings are responsible to spalling of protective oxide scales. The most widely used coatings are diffusion coatings, modified diffusion coating, overlayer coating and thermal barrier coatings.

2. 1. Diffusion Coatings

The use of protective coatings in industrial engines began with the introduction of chromium coatings in

the 1960s, although aluminide coatings had been employed previously in marine gas turbines. Chromium diffusion coatings give the best results when compared with aluminising, the Pt-Al coating, the Ti-Si coating and MCrAlY overlayer coating-types (Grünling and Schneider, 1981; Goward, 1986; Bürgel, 1986; Van and Hsu, 1989; Bhushn and Gupt, 1991).

The Ni Cr Si coating was exploited by manufacturers and should replace chromium coatings. The advantage of this coating is that the atmospheric-pressure plasma sprayed NiCrSi coating (especially with silicon-rich coatings) represents a good compromise achieved between corrosion resistance and mechanical properties (Grünling and Schneider, 1981; Bürgel, 1986; Stringer, 1997).

Diffusion coatings used for high temperature service are generally aluminides obtained by pack cementation. The most developed pack cementation processes include aluminising, chromising and siliconizing (Goward, 1986; Hancock, 1986; Mevrel et all., 1986; Restall and Wood, 1986; Radcliff, 1997). Pack cementation is relatively simple techniques which consists of immersing the components to be coated in a powder mixture. Two different types of the process can be employed: low activity and high activity. In the former process, the aluminide coating is formed by outward diffusion of the aluminium and subsequent heat treatment. Normally the high activity process is preferred: this produces a coating with good oxidation resistance, but poor hot corrosion performance. The hot corrosion resistance is improved by changing the composition of the coating by the addition of elements such as chromium and/or platinum (Bürgel, 1986; Mevrel et all., 1986; Radcliff, 1997). Figure 5 shows aluminide coating microstructure obtained the high activity pack cementation. Three typical zone are illustrated in Figure 5.
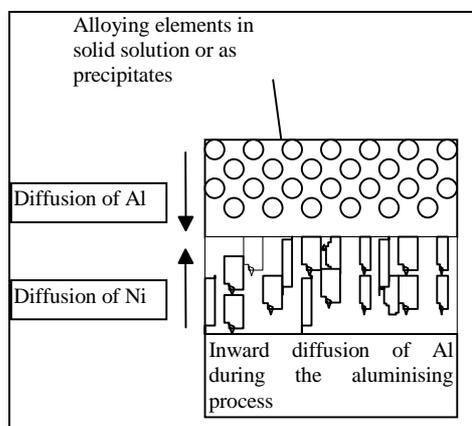

Figure 5. Pack cementation aluminide coating microstructure (Restall and Wood, 1986)

2. 2. Modified Diffusion Coatings

Diffusion aluminide coatings represent good oxidation resistance, but poor hot corrosion performance. The improved oxygen and sulphate hot corrosion resistance is achieved by modifying the coating (Schneider, 1981; Bürgel, 1986; Grünling and Goward, 1986; Meetham, 1986; Mevrel et all., 1986; Rhys-Jones, 1989; Van, Roode and Hsu, 1989; Anon, 1990; Tabakoff and Metwally, 1992; Radcliff, 1997).

Two modifier elements are commonly used in aluminide coatings: chromium and platinum. The addition of platinum to diffusion aluminide coatings improved the resistance of these coatings to high temperature hot corrosion and low temperature hot corrosion. Platinum-modified aluminide coatings such as LDC2 and RT22 which are used for erosion and corrosion/oxidation protection of hot section component have gained importance, particularly in aero turbines, marine operation and in land-based engines. The major disadvantages of the platinum-modified coatings are their high cost and limited ductility. The limited ductility of the coatings can lead to thermal cracking in service (Bürgel, 1986; Mevrel et all., 1986; Stephenson, 1989; Tbakaoff et all., 1992).

The addition of chromium is to improve the hot corrosion resistance of nickel base alloys. Chromium enrichment of a surface layer on the low-chromium substrate materials is generally obtained by a chromizing treatment (either pack cementation or a gas-phase processes).

2. 3. Overlayer Coating

Overlayer coatings can be applied by electron beam vapour deposition, sputtering, plasma spraying and various other techniques (Grünling and Schneider, 1981; Booth and Clarke, 1986; Meetham, 1986; Mevrel et all., 1986; Rhys-Jones, 1989; Sivackumar and Mordike, 1989; Van and Hsu, 1989; Ari-Gur et all., 1991; Bhushn and Gupt, 1991; Tabakaoffet all., 1992; Tabakoff and Metwally, 1992; Stringer, 1997).

Overlayer coatings which have general formulation MCrAlY (where M = Ni, Co, Fe or combination there of) have been exploited to withstand hot corrosion. The compositional limitation of the aluminides, as explained above, when deposited by pack commendation can be overcome by using overlayer coatings of the MCrAlY type. Further

ingredients can be added to obtain special properties. It was reported in the literature (Mevrel et all., 1986; Sivackumar and Mordike, 1989) that CoCrAlY coatings with high chromium content offer further protection than the NiCrAlY overlayer coating types. MCrAlY coatings include yittrium to improve the adherence of the protective Al_2O_3 scale and the sulphidation resistance (Grünling and Schneider, 1981; Goward, 1986; Sivackumar and Mordike, 1989; Ari-Gur, et all., 1991; Stringer, 1997). The MCrAlY coatings are employed in aero engines, industrial and marine aircraft engines.

Furthermore, although the main reason for coating on hot section component is to extend its lifetime by increasing its hot corrosion resistance, other important properties such as creep and fatigue also can be modified by applying a coating. An appropriate coating applied improve the resistance to fatigue and creep. MCrAlY overlayer coatings have higher thermal fatigue resistance than that of diffusion aluminide coatings.

2. 4. Thermal Barrier Coatings (TBC's)

TBC's which act as thermal barrier between hot combustion gas and the turbine metal surface are used on turbine gas path surfaces to reduce metal temperatures and minimise component distortion, cracking and to increase thermal shock resistance as well as the corrosion resistance, and thereby extend the lifetimes of hot section (Grünling and Schneider, 1981; Vogan et all., 1981; Goward, 1986; Meetham, 1986; Sivackumar and Mordike, 1989; Bhushn and Gupt, 1991; Mier, Nissley, Sheeffler and Cruse, 1992; Strangman, 1992; Radcliff, 1997; Almaida and Montez, 1997).

TBC's such as an inner bondcoat layer of Ni-Cr-Al-Y and Co-Cr-Al-Y and then an insulative stabilised zirconia outer layer (Y_2O_3-ZrO_2) are generally applied by plasma spraying. TBC's consist of ceramic with low thermal conductivities. Zirconia is the preferred ceramic because of its extremely low conductivity; however additions of Y_2O_3, CaO or MgO are required to prevent phase transformations during thermal cycling. Yittria-stabilized zirconia is considered to have good oxidation and hot corrosion resistance. G. W. MEETHAM (Meetham, 1986) shown that two layer partially yittria-stabilized zirconia/MCrAlY coating has much improved thermal fatigue resistance.

The metallic MCrAlY bond layer under the ceramic coatings (Figure 6) improves the major problem of spallation sensitivy due to the difference in the thermal expansion between the coating and the

substrate (Grünling and Schneider, 1981; Vogan et all., 1981; Wortman, et al., 1989; Almaida and Montez, 1997). The requirements for bondcoat and ceramic overlayer are listed in Table 2 (Bhushn and Gupt, 1991).
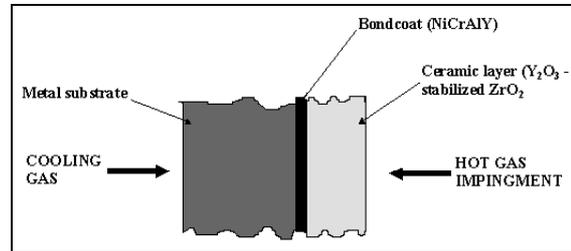

Figure 6. Representation thermal barrier structure (Bhushn and Gupt, 1991)

Table 2. Requirements for High Temperature Coatings (Bhushn and Gupt, 1991)

Ceramic Coating Layer
Strain accommodation
Stability in gas environment
Low thermal conductivity
Good adhesion with metallic
Coating
Metallic Coating Layer
Good diffusion stability with substrate alloy

3. CONCLUSION

Coatings for different applications have been successfully used in industrial gas turbines for about two decades. Coatings offer a simple method of changing or improving the chemical, mechanical and even thermal surface properties of materials and components. The various types of protective coating used in the turbine engines operating are reviewed in this papers. The factors affecting coating selection for turbine applications are discussed, and service conditions are reviewed.

Aluminide coatings provide good protection on many turbine components. In many cases MCrAlY and platinium-aluminide coats can provide the improved corrosion protection. Thermal barrier coating systems have made progress to obtain high thermal fatigue resistance in turbine applications. Table 3 gives a summary of the coating developments which are related to an interaction between the physical metallurgy of the coating and the processing for turbine components.

Table 3. Coatings For Turbine Components

Coating Type	Coating Method	Coating Phase	Limitation
Diffusion	Pack aluminizing	NiAl	Hot Corrosion Brittleness Diffusional stability
Overlay	Electron beam evaporation	MCrAlY	Hot corrosion Thermal Fatigue
Overlay	Low pressure Plasma spraying	MCrAlY	Hot corrosion Thermal Fatigue
Thermal barrier	Air plasma spraying Electron beam processes	Partially stabilized ZrO_2	Thermal spalling, oxidation and hot corrosion of bondcoat

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