Journal of Environmental Protection, Safety, Education and Management
2013, Number 2, Volume 1, date of issue 28th November 2013 ISSN 1339-5270

INCREASING THE EFFICIENCY OF STATIONARY GAS TURBINES THROUGH MODERN COATING SYSTEMS

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Abstract

It is possible to increase the efficiency by raising the inlet temperatures. Since even such state-of-the-art materials as monocrystalline alloys reach their limits at such temperatures, these materials have to be protected with appropriate coatings; in particular, thermal barrier coatings. The energy cycle of an engine also is optimized due to reductions in the cooling air.

Key words
Gas turbines, Coating systems, New coating architectures, Thermal barrier coatings, Thermally-grown oxide coating

1. Introduction

One of the ambitious objectives of our times is to meet the ceaselessly growing demand for energy around the globe while also considering the much discussed related environmental and climatic problems.

Just to supply electric power, new utilities for generating 5,000 GW of power have to be newly installed by 2030. To date, this enormous demand for energy can only be supplied through fossil-fired, conventional power plants if the efforts undertaken to abandon nuclear energy are to be advanced further. According to the Kyoto Protocol, however, CO_2 emissions have to be reduced significantly. That is why natural gas assumes a vital role. When one considers that natural gas produces only 70% of the CO_2 emitted by hard coal and 90% of the CO_2 released by fuel oil in the production of the same amount of energy, then this indicates a potential which can be tapped within a short period as well as medium period of time. [1]

It is possible to increase the efficiency by raising the inlet temperatures. Since even such state-of-the-art materials as monocrystalline alloys reach their limits at such temperatures, these materials have to be protected with appropriate coatings; in particular, thermal barrier coatings (TBC). The energy cycle of an engine also is optimized due to reductions in the cooling air.

2. Background History and State of Technology

Already around 1955, the development of thermal barrier coatings began with the first enamel coatings on components of military aircraft turbines. The first commercial aircraft engines with flame-sprayed ceramic coatings were used in the early 1960s.

During the subsequent years, the systems were constantly improved with the help of better material properties and coating technologies.

During the early 1980s, zircon oxide with partially stabilized yttrium oxide – the so-called yttria-stabilized zirconia (YSZ) – was identified as an outstanding coating material which, in conjunction with bond and corrosion protection coatings (BCC), has remained the standard method for coating turbine parts until today. [2]
The combination of bonding and coating layers is also referred to as the duplex system. Figure 1 depicts a coated turbine blade. Figure 2 shows the schematic temperature profile of such a coating system.

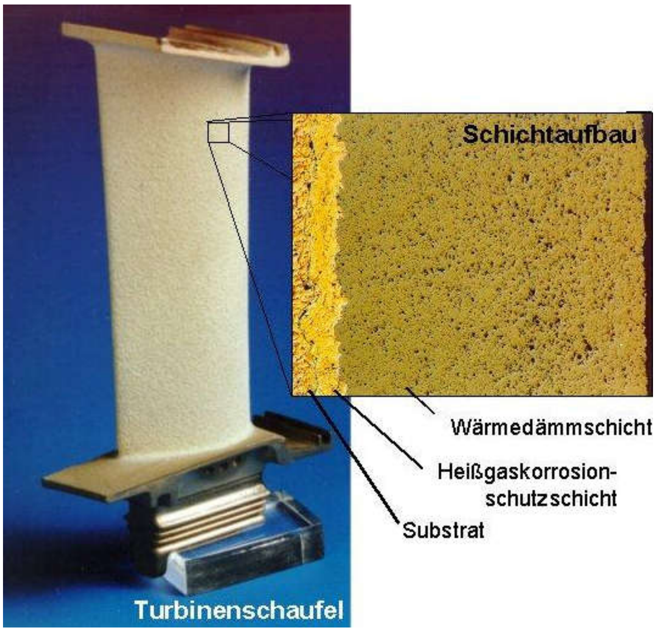

Figure 1: Layer Structure [13]

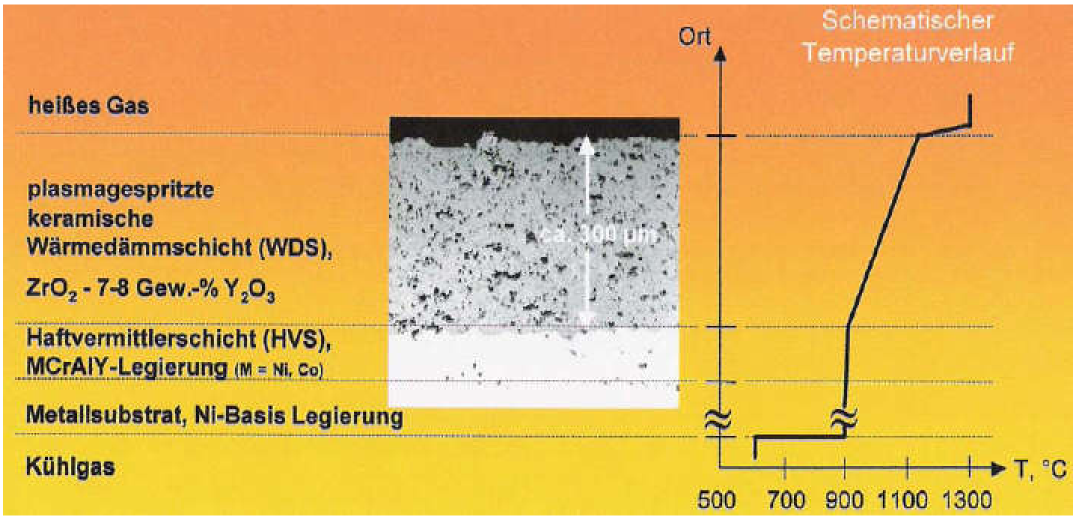

Figure 2: Schematic Temperature Profile [14]

The bonding layers from the 1950s and 1960s were based on such simple alloys as NiCr or NiAl which were applied on the substrates during flame spraying. These bonding layers have been continuously developed since those days. Today's NiCoCrAlY layers exhibit improved oxidation and corrosion protection properties. [2]

3. Production Procedure

Both layers of the duplex system are mostly applied with thermal spraying procedures. Modern thermal spraying surface technology permits a number of different applications. Layers to increase the corrosion protection as well as the wear and tear protection, or insulating layers to protect, for example, against electric power or heat, may be applied to numerous substrate materials. Spray coatings consist of refractory metals, ceramics, or oxides. Depending on which spraying method is selected, the spraying material (e.g. as a powder) is introduced into a high energy thermal source (e.g. plasma), melted, and applied to the substrate at a high speed. That is where the spray coating is formed. The workpiece to be coated is only exposed to limited thermal stress. [3]

There are a number of thermal spraying procedures in use. The layers described herein were produced with the high velocity flame spraying (HVOF), the atmospheric plasma spraying (APS), and the vacuum plasma spraying (VPS) procedures. In the HVOF (high velocity oxygen fuel) procedure, a mixture of combustible gas and oxygen is ignited in the combustion chamber. By adding large amounts of gas, it is possible to produce very high pressure in the combustion chamber. [4]

Via a powder conveyor, the spray powder reaches the water cooled expansion nozzle centrally and axially, is melted, and accelerated considerably. At a flame speed of up to 2,000 m/s, for example, Al_2O_3 particles having a size of 5 µm can reach a speed of 1,200 m/s. [3]

HVOF layers excel with their good bonding strength, high density, and premium surface quality. [5]

Plasma spraying is one of the latest thermal spraying procedures and is, at the same time, considered to be the most universal procedure. It is actually a byproduct of aeronautical and aerospace technology research. The high enthalpy of the plasma jet permits not only the spraying of metallic, but also such refractory materials as nitrides, borides, carbides, and oxide ceramics onto a substrate. These materials are typically processed as powders. It is essential that the spray powder melts completely. That is why such ceramics as SiC, which decompose thermally, cannot be processed through APS. During plasma spraying, an electric arc is generated between an anodic, water cooled nozzle (often made from copper) and a wolfram cathode through high frequency ignition. A gaseous mixture and/or pure gases such as Ar or He flow through the electric arc. The heating, partial ionization, and dissociation of the gas creates a plasma jet. The spray powder is fed through boreholes into the plasma flame with the help of a carrier gas, then brought to melting, and cast onto the substrate where the spray coating is formed. [5]

The development of the VPS procedure resulted from the demand for coating systems with a better quality. With this spraying procedure, it is possible to avoid oxide inclusions, porosities, and the associated poor bonding strength, for example, in hot gas corrosion protection layers of the MCrAlY type (where M stands for the elements Ni and/or Co). Materials which have a high affinity towards O_2 or N_2, such as Ti and Ta, may also be suitable. A vacuum plasma spraying system has a vacuum chamber that has an approximate size of 2 m^3 to 3 m^3. This chamber has to be evacuated prior to starting the spraying process. The spraying is carried out at a pressure ranging between 20 hPa and 200 hPa. The high speed of the spraying particles, which can reach up to 800 m/s, is considered to be the characterisitc feature of this procedure. This is due to the low porosity of the spray coating which can be less than 1 %. [6]

4. The Classic TBC System

The classic TBC system consists of both a bond coating and the actual functional coating layer. The bonding layer or bond coating (BCC) essentially has to accomplish two primary tasks. On the one hand, it ensures that the ceramic TBC adheres well to the metallic substrate and, on the other hand, it protects the substrate from high temperature oxidation and high temperature corrosion. Plasma sprayed TBC have open porosity. In addition, ZrO_2 is oxygen ion conductive so that virtually no oxidation protection exists for the metal substrate. With the corresponding BCC, oxidation occurs between the bonding layer and the thermal barrier coating. Today, MCrAlY alloys are state-of-the-art for BCC. M represents the elements Ni and/or Co. The relationship of these two elements determines the ductility and the creep properties of the bonding layer.[7]

The aluminum content often amounts to approx. 10 wt. % when creating an aluminum oxide layer, the so-called thermally grown oxide layer (TGO). This layer acts as an oxidation barrier. The reactive element yttrium further reduces, for example, the oxidation rate. However, if the Y content is too high, an internal oxidation will occur in the bonding layer which would, in turn, increase the oxidation rate. Y contents between 0.1 wt. % and 0.5 wt. % are considered to be favorable. [2]

As a general principle, the composition of BCC has to be adjusted to the substrate material which is to be coated. As to the life span of BCC, the application with vacuum plasma spraying is considered to be the most favorable method because atmospherically sprayed bonding layers undergo preliminary oxidation during the production process. [7]

The more inexpensive high speed flame spraying procedure has been used increasingly over the past few years. Even though these coatings have an increased oxygen content, they exhibit good oxidation behavior due to the homogeneous distribution of Al_2O_3 particles. With all procedures, the layer thickness typically reaches about 100 µm. This layer thickness suffices for the BCC to function. If the overlying thermal barrier coating is applied with atmospheric plasma spraying, then the BCC's surface finish has to be sufficiently rough to permit the adhesion of this thermal barrier coating because adhesion is primarily due to mechanical interlocking. This roughness depends on the particle size of the applied spray powder and the spray parameters which were set on the coating system. Normally, the roughness coefficients R_a are between 5 µm and 15 µm. [2]

Recapitulating, BCC makes a decisive contribution to the life span of a TBC system. But it is very complex and still not entirely understood. That is why it is necessary to analyze the thermomechanical behavior of BCC interlayer bonding more precisely in the future. [7]

The actual functional layer within the TBC system consists of YSZ. Zircon oxide belongs to the group of oxidic, ceramic materials; and it specifically excels with great hardness. ZrO_2 changes its morphology when it is heated or cooled. The reversible tetragonal-monoclinic phase transition is accompanied by an approx. 5 % to 8 % increase in volume. This results in formed pieces bursting during cooling after the sintering process.

It is possible to keep the tetragonal and/or cubic phase metastable and to even stabilize it at room temperature when applying a doping material containing a stabilizer, for example, yttrium oxide Y_2O_3. In manufacturing, partially stabilized zircon oxide is used as a thermal barrier coating material. It is generated through the introduction of Y_2O_3 into the ZrO_2 structure during the firing when the pieces are produced, and it stays stable up to approx. 1,200 °C. [8]

5. The limitations of use and the failure of classical thermal insulation coating systems

The failure of a thermal insulation coating system usually expresses itself in the peeling off of the coatings and usually results in the failure of the component concerned. Although the different possible operating temperatures have been taken into account, the cause is to be located in the thermo-mechanical stress to which the coating system has been subject. Different thermal expansion coefficients and bond strengths of the individual components lead to tension in the coatings and the substrate. This situation is added to by residual stresses which result from the coating procedure. The level of residual stress is dependent on a number of parameters such as the characteristics of the materials used, the component geometry and the coating thicknesses to be achieved. The workpiece is warmed during the passage of the spray burner over its surface via the impact of the hot spray particles and the flame jet. Heat is transferred to the substrate when the coating put on it solidifies. This results in expansion of the workpiece. The components of the coating system and the substrate cool at different rates after the spraying process. [10]

The thermally-grown oxide coating (TGO) exercises a decisive influence on the failure of a thermal insulation coating system. In addition to the failure within the thermal insulation coating close to the bond coat, APS thermal insulation coatings often experience a failure of the TGO itself. The oxide growth of the bond coat and its roughness are significant factors for the tension state in the coating system. [2]

At this point, it is also necessary to point to the influence of the substrate geometry. If the workpiece is to be coated on a curved surface, in addition to the tensile and compressive stresses outlined above, additional tensile stresses occur in a radial direction. [2]

The failure of the thermal insulation coating system has developed into the most important criterion in making life-expectancy estimations for such coatings. This explains why thermal cycle tests place such an important role in investigations of thermal insulation coatings.

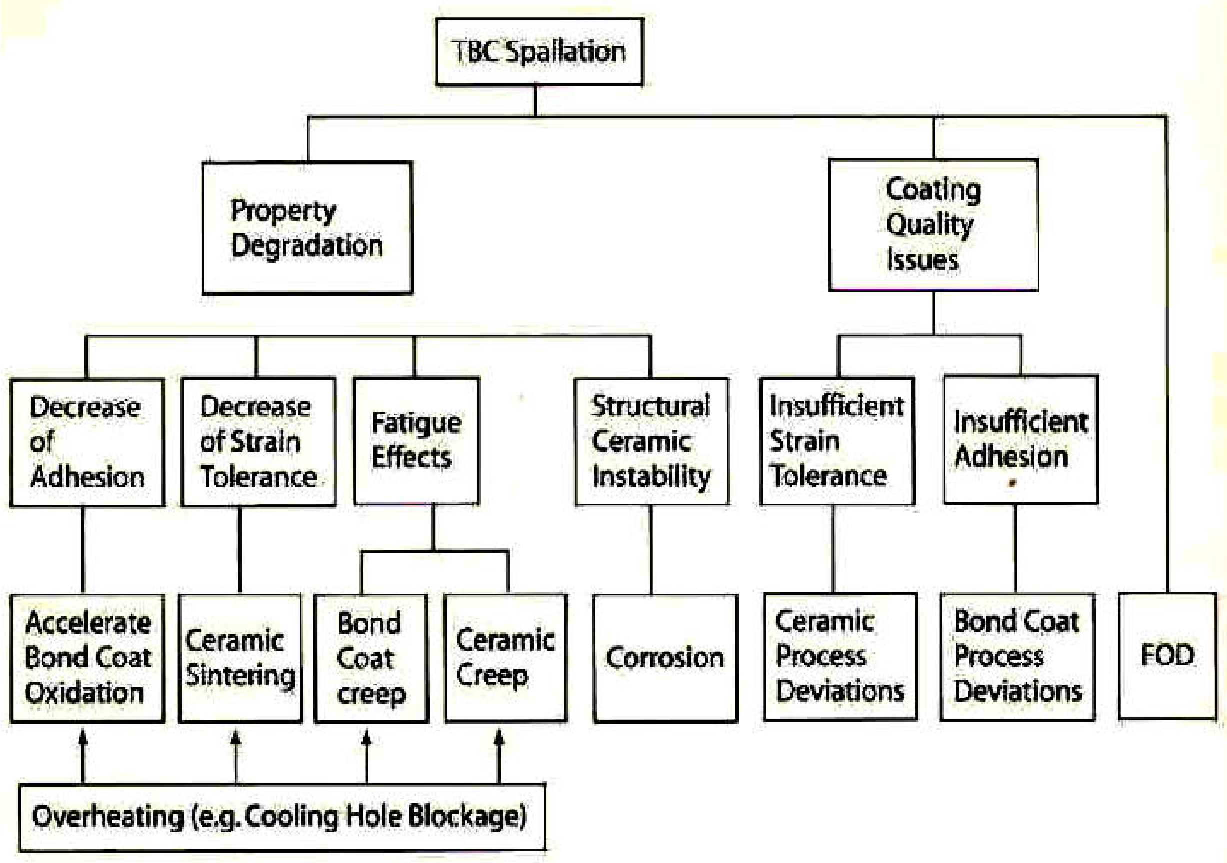

Figure 3: TBC failure overview [15]

6. New TBC Systems

In addition to finding new materials, a number of attempts were also undertaken to improve classic YSZ over the past few years. These measures sought to improve the tendency to sinter by reducing the impurities of YSZ. These attempts encountered, though, natural limits.

Another approach is to dope the zircon oxide with other additives to increase phase stability. This was achieved, for example, with Sc_2O_3 and other rare-earth oxides. Such additives as 4 mol. % of Nd_2O_3, Gd_2O_3, and others actually did result in lower thermal conductivity; in other words, improved insulation.

Long-term studies, such as furnace tests, however, found neither sufficient stability nor any other improved properties when compared to YSZ. When selecting new TBC materials as an alternative to YSZ, numerous criteria need to be observed.

Suitable materials need to have good oxidation resistance when they are used in gas turbines because the excess air produces higher partial oxygen pressure in the combustion chamber and the exhaust gases. Phase stability at the place of application, combined with reduced sintering properties, is decisive for the life span of a layer. The highest possible melting point of a material has to be considered in this context as well because it indicates great temperature resistance.
Low thermal conductivity is necessary for thermal barrier coating. Fewer good values can be compensated through the appropriate coating thickness. But this increases the weight considerably which is undesirable, for example, in moving blades. Thick layers reduce the thermomechanical properties of spray coatings which, in turn, is contingent on the place of application.

The various thermal expansion coefficients are decisive for the thermomechanical characteristics of a coating system because they produce stress in the interlayer bonding. The TBC thermal expansion coefficient should, therefore, be as high as possible and ought to be in the substrate material range and/or the BCC. Good thermocyclic characteristics are also necessary since they indicate a long life span for the coating system.

Depending on the field of application, new TBC materials need to have sufficient chemical stability as well as good corrosion and erosion protection. The most recent research has focused on oxides which are characterized by a very high melting point and a perovskite and/or pyrochlorite structure. The mineral perovskite ($CaTiO_3$) with its typical structure classifies an entire material category which is described by the chemical molecular formula ABO_3.

The structure varies, though, depending on the cation radius. The middle of the surface is occupied by oxygen ions having edges and/or corners with larger cations while the center is occupied by smaller cations. Numerous perovskites, though, have also orthorhombic or tetragonal structures. Perovskites are already used in electrical engineering so that a large body of knowledge is available on this particular material. In the search for suitable thermal barrier coating materials, perovskite strontium zirconite and barium zirconite seem to be promising because they have very high melting points. Table 1 summarizes the essential properties of $BaZrO_3$. [2]

Property	$BaZrO_3$
Melting Point [°C]	2,690
Thermal Conductivity [W/mK]	3.4
Thermal Expansion Coefficient [1 E-6/K]	8.5

Table 1: Properties of $BaZrO_3$ [2]

Pyrochlorite refers to a type of crystal lattice which has the structure of the mineral bearing the same name

$$(NaCa)(NbTa)O_6F/(OH).$$

It refers to a cubic structure which has 8 molecules per unit cell. [9] A number of publications describe, for example, experiments with lanthanum zirconite as a possible new TBC material.

To increase the efficiency of thermal barrier coating systems, a new material in and by itself, though, is not enough to meet the increased specifications and requirements. Concentrated and multilayered coating systems were developed and tested to improve the thermomechanical properties and to reduce the stress in the interlayer bonding.

Concentrated coating systems are characterized by a continuous transition from the metallic bonding layer to the ceramic thermal barrier coating. This permits an adjustment to the most diverse thermal expansion coefficients and, thus, results in higher stability during thermocyclic stress. [11] This should also result in a longer life span.
Thermal barrier coatings have to face considerable stress in form of hot gas corrosion, oxidation, or thermal shock. That is why attempts are undertaken to create multilayer systems in which the individual layers fulfill different functions. [11] A simple multilayer system is the classic duplex system in which the BCC provides the adhesion to the metal substrate and provides protection against corrosion and oxidation while the TBC is primarily responsible for thermal insulation. Additional layers are also conceivable, for example, as diffusion barriers or sealants.

Even when new thermal barrier coating materials are used, the retention of at least one classic YSZ layer is often described because this is typically tougher and has a higher expansion coefficient. [2]

But many layers can result in bonding problems between the layers which can lead to failure in the interlayer bonding. That is why it is essential to always keep the number of layers as small as possible. It is even possible that a layer can assume multiple functions if the right material is selected. A combination of multiple layers and concentrated coatings can also extend the life span.

Thermally sprayed layers often cannot fulfill all of the specifications. This is primarily due to the insufficient coating structure as well as too much porosity. A specific finishing treatment applied after the spraying process can significantly increase the coating characteristics through homogenization and/or sealants particularly for those sections which are close to the surface. [12]

The sol-gel procedure, for example, and CO_2 laser sealing are possible sealing technologies.

The essential objectives include [12]:

- Reducing layer porosity
- Avoiding layer seepage
- Improved surface structure
- Reducing internal stress

7. Conclusion

Current coating systems used in gas turbines demonstrate stability up to 1,200 °C. In order to realize a significant increase in efficiency, it would suffice if the inlet gas temperature is increased by 110 K to 150 K. At even higher temperatures, unwanted nitric oxides are produced as exhaust gases. New coating architectures, such as graded coatings and sealings, have to be used in addition to new materials. First experiments indicate promising results. The decisive criterion during the testing of new coatings is the ability to withstand thermal shock because these measurements come close to exacting operational conditions and, thus, permit reliable conclusions to be drawn for the life span.

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2013, Number 2, Volume 1, date of issue 28th November 2013
ISSN 1339-5270

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