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Coatings for Superalloys

Mathias C. Galetz

Abstract

High-temperature coatings for superalloys can be divided into three categories: Two of them, diffusion and overlay coatings, are both used to protect a system from oxidation and corrosion. The third type, thermal barrier coatings, protects the substrate from thermal degradation.

All types of coatings are designed to avoid direct contact between a hot gas or detrimental components from the environment and the base metal alloy. The aim is to enhance the lifetime of high temperature applications, which is otherwise often limited by corrosion or thermal degradation. In this chapter, the different coatings and their durability are discussed, which ideally matches the aging process of the substrate underneath. Besides the corrosive attack the coatings must also often be able to withstand certain mechanical and thermal mechanical loads as well as erosion. Nevertheless, all coatings have a limited thickness and get consumed in service. Therefore it is essential to understand and choose coatings that show slow degradation mechanisms.

Keywords: Diffusion coatings, MCrAlYs, TBC

1. Introduction

Superalloys are operated in industrial environments containing corrosive species such as sulfur, chlorine- or carbon-containing compounds, water vapor, alkali and alkaline-earth metal salts, or ashes such as vanadates [1,2]. At elevated temperatures, such compounds cause a wide range of attack types on most metallic alloys such as oxidation, carburization, sulfidation, hot

corrosion, or a combination of different mechanisms [3,4]. But even in air the oxidation resistance of nickel- and cobalt-based superalloys is not sufficient for continuous operation above 1000°C [5]. Oxide scales grow too fast and the subsurface zone of the alloys is changed and loses its mechanical strength [6-8]. Despite these limitations, advances and improvements of industrial technology have led to more efficient processes and more powerful engines with increased operation temperatures, and the alloys used for their construction are pushed toward the applicable limit even as far as mechanical properties are concerned, such as fatigue, tensile strength, and creep resistance [9]. Therefore higher additions of alloying elements for corrosion protection such as Cr, Al, or Si cannot be used as they either lead to embrittlement or lower the melting point and therefore the creep strength at the high target temperatures [10,11]. The only way is to apply high-temperature coatings to face aggressive corrosive high-temperature atmospheres and make processes possible which could not be operated efficiently and reliably without such coatings.

Diffusion- and metal-based overlay coatings are both used to protect a system from oxidation and corrosion [12]. Such coatings are designed to avoid direct contact between the base metal alloy and a hot gas carrying detrimental species by growing a thin, self-healing oxide scale in situ.

Besides oxidation and corrosion protection, the other major factor affecting the overall life of substrates at high temperatures are heat-flux effects. Nickel- and cobalt-based alloys are employed in gas temperatures up to 1400°C [13]. Without proper protection, the temperatures could easily induce softening or even reach the melting point of the alloys. The employed materials are the actual major constraints that determine the maximum gas temperatures in many processes of today's aircraft as well as energy conversion industry. Without cooling and protection by coatings, the efficiency and speed of jet engines would also be limited to a very low level. In these cases, only a combination of two coatings allows operation; a so-called bond coat (the bond coat belongs to the class of diffusion or overlay coatings, which are discussed in detail below) in combination with a ceramic layer on top to form a thermal barrier coating system. The ceramic layer also reduces the attack indirectly by lowering the metal surface temperature and thus decelerates the degradation of the metallic coating and substrate underneath.
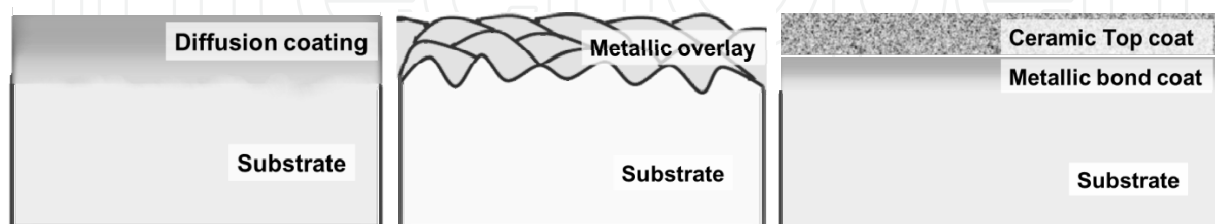

Figure 1. Schematic sketches of the general configuration of the three different types of coatings used for high-temperature applications (from left to right): diffusion coatings, metal overlay coatings, and thermal barrier coatings

Only by combining one of the different types of coatings schematically shown in Figure 1 with a load-carrying superalloy underneath, safe operation over a reasonable lifetime can be

ensured. In operation the coatings must be able to sustain certain mechanical and thermo-mechanical loads as well as erosion on top of the oxidative or corrosive attack. Ideally, the durability or lifetime of protective coatings for parts such as turbine blades or vanes matches that of the aging processes of the substrate underneath. However, since all coatings are more or less thin films, the mechanical lifetime of the substrate is often longer than the period of coating degradation at high temperature. Therefore, after a certain time in service, the coatings residues are stripped and the coatings are remanufactured several times during the lifetime of the blades [14].

2. Requirements for protective coatings at high temperatures

Unlike aqueous corrosion conditions at low temperatures, where usually either an anodic protection is applied or even very thin barrier coatings can protect from degradation by separating an electrolyte from the material, high-temperature degradation processes are controlled by transport processes in or through coatings via diffusion. High temperatures are especially demanding because all metals tend to become thermodynamically stable in their oxidized form or tend to react with other gas components such as nitrogen, carbon, or sulfur. For example, even highly corrosion-resistant platinum suffers from significant oxidative degradation above 1000°C in air [15]. Which corrosion products form in an environment depends on the partial pressure or activity of different potential reaction partners in the atmosphere. The idea behind all oxidation- and corrosion-resistant coatings is to create a reservoir of scale-forming elements from which a thermodynamically stable, slow growing, adherent scale can be formed, consisting of corrosion products, usually thermally grown oxide on the surface. An overview of the requirements for coatings for high temperatures is provided in Table 1.

• Slow-growing, thermodynamically stable scale formation and high concentration of the scale-forming elements

• Thermal stability, no detrimental phase changes

• Erosion resistance

• Good adhesion

• Low interdiffusion of the substrate

• Mechanical compatibility: similar modulus and thermal expansion to avoid stresses at the interface

• No crack initiation, not too brittle

• Good processability

• Low price

Table 1. Requirements for high-temperature coatings

Even with stable protective oxide scales, the service conditions will usually create flaws such as cracks in the scale. Most important is the self-healing potential or ability for reformation, properties which for example a pure ceramic coating cannot provide. In Figure 2 a pure ceramic coating is compared with a thermally grown oxide scale that builds up in situ. In the first case,

if a crack occurs, the atmosphere can attack the metal below, which cannot protect itself. Ceramics also always possess a certain porosity and cannot prevent the gas from reaching the metal below, which means they offer no effective long-term corrosion protection. Ceramic coatings are therefore almost exclusively used to lower substrate temperatures and in combination with one additional coating of the diffusion or metallic overlay type which can form slow-growing oxides. Diffusion or overlay coatings possess a sufficient reservoir of protective elements underneath the scale to allow the reformation of the protective scale many times before the reservoir of the protective elements is depleted.
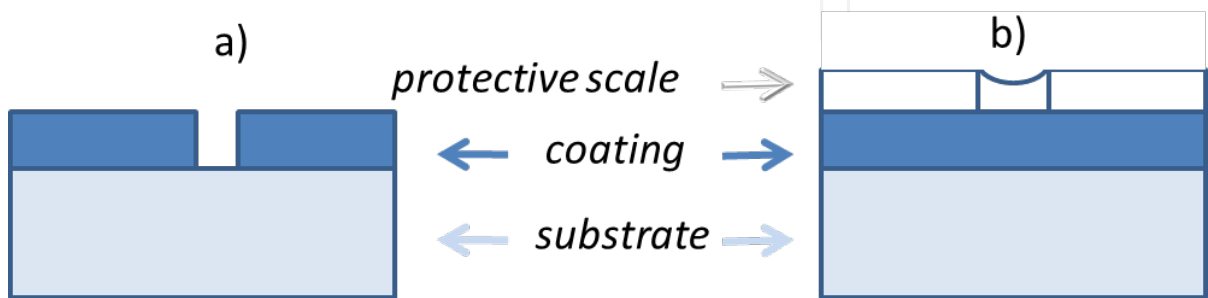

Figure 2. Comparison between a ceramic coating without self-healing properties (a) and a reservoir coating that allows the reestablishing of the protective scale in case of local failure (b)

The potentially protective elements, which qualify for scale formation, must form thermodynamically more stable corrosion products than the main elements in the superalloy such as nickel or cobalt. The graph in Figure 3 is a simplified Ellingham-Richardson Diagram that shows the standard free energy of oxide formation as a function of the temperature. Generally, for scale formation on nickel- or cobalt-based alloys, elements with a very high affinity to oxygen such as aluminum, chromium, or silicon are important, but also titanium or tantalum would theoretically qualify. The drawback for example in the case of titanium is that it allows fast oxygen diffusion through its oxide scales, which have high growth rates even at moderate temperatures. Additionally, they often tend to spall off easily.

So not only the criterion of thermodynamically preferred reaction has to be fulfilled, the scales also have to be slow-growing. Only scales that form a dense and stable crystal lattice effectively limit diffusion and guarantee a slow growth and weight gain as shown in Figure 4. From the curve, the growth rate constant k_p of the thermally growing oxide can be determined according to the function:

$$(\Delta m)^n = k_p t \tag{1}$$

where Δm is the weight gain per surface area of the metal [g/cm^2], t is the exposure time [s], and n is the rate exponent. If the scale is protective, stable, and adherent, the value of n is usually close to 2 and the weight gain shows a parabolic diffusion-controlled behavior. The diffusion is generated by the anion and cation concentration gradient in the scale. The speed
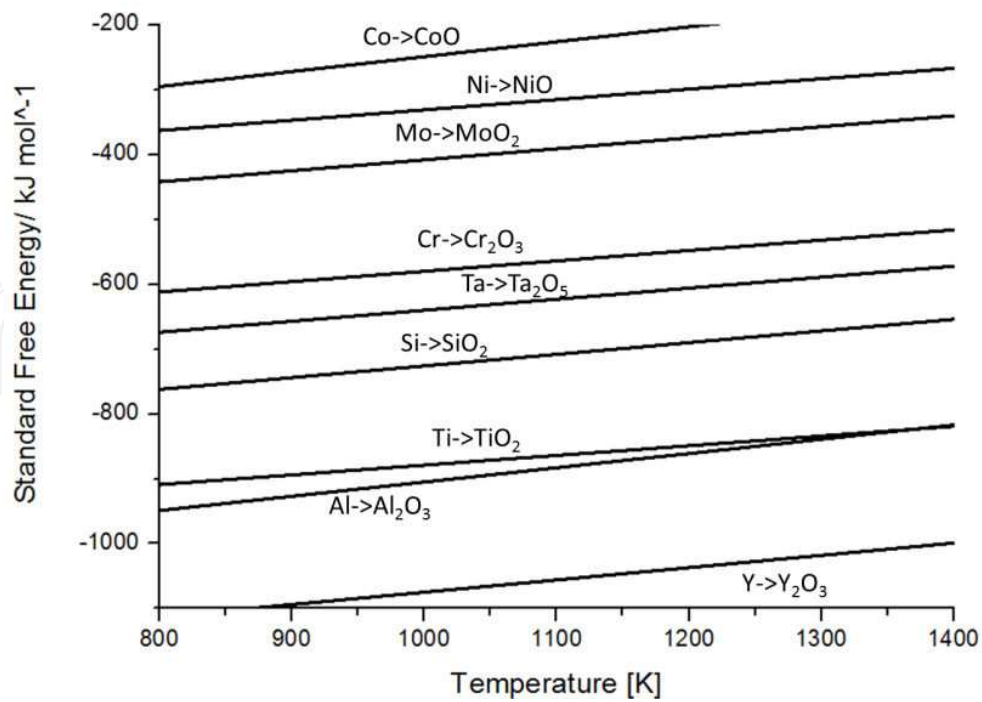
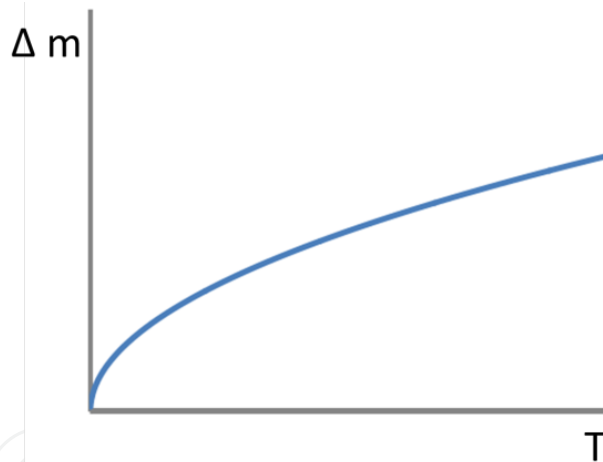**Figure 3.** Simplified Ellingham-Richardson Diagram

Figure 4. Parabolic weight gain of ideal scale growth

of diffusion is determined by the crystallographic structure of the oxide, the defect structure, and the microstructure, for example grain size and grain boundary distribution. In most cases, the faster diffusing species is a metallic cation, but anion diffusion is also possible [16], for example it is predominant in silica formers in a wide range of temperatures. Figure 5 shows the parabolic rate constants at 1000°C normalized to the behavior of slow-growing alumina for nickel, chromium, and silicon. It can be seen that Cr, Al, and Si offer much slower growth rates than the base metal nickel. Cobalt is not included in the diagram since its oxidation rate is even ten times higher than that of nickel.
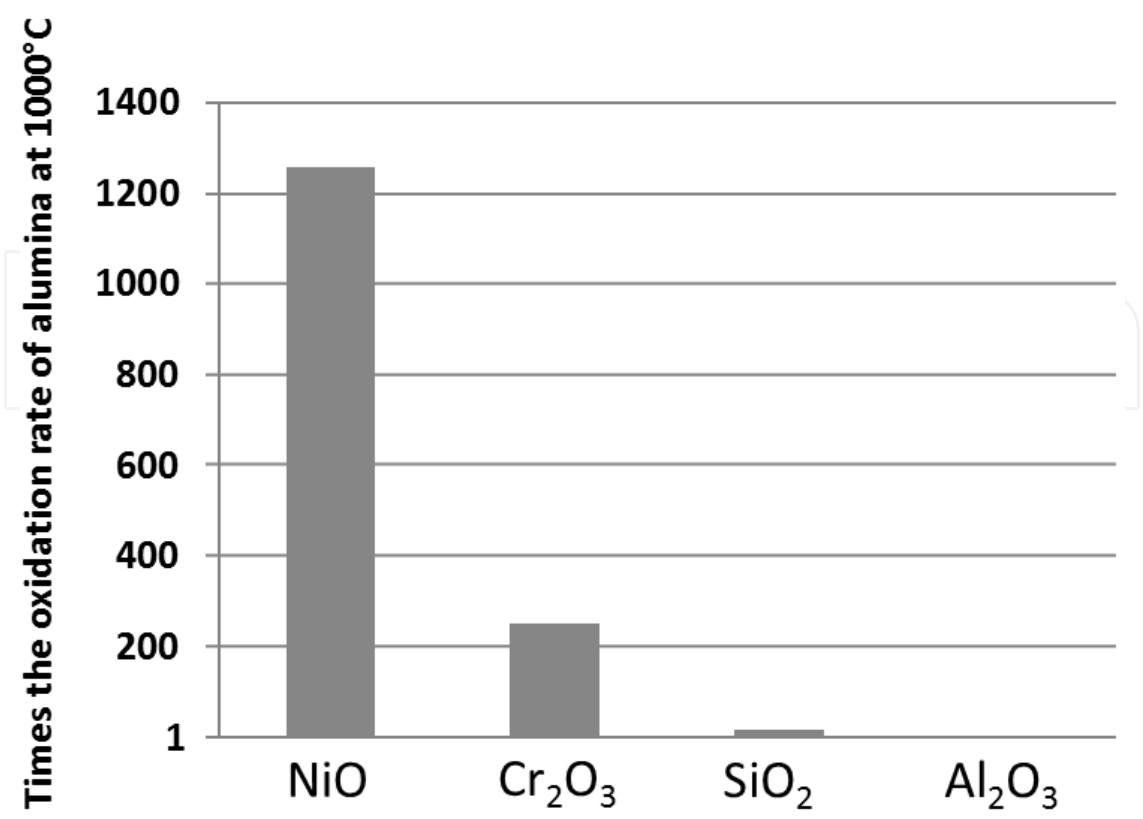
Figure 5. Parabolic rate constants of Fe, Co, Ni, Cr, Si, and Al oxide formers at 1000°C; data from [17] as k_p ($g^2cm^{-4}s^{-2}$)

Further requirements derive from the mechanical interaction of the scale with the coating underneath. During formation growth stresses occur due to the volume change, when a scale is formed by including elements from the environment such as oxygen. As a first hint on the stresses, the classical approach of Pilling and Bedworth from 1923 can be used, according to which the Pilling-Bedworth Ratio is defined as:

$$PBR_{metal} = \frac{Volume\ of\ oxide}{Volume\ of\ metal}$$

(2)

It must be higher than 1 in order to guarantee a continuous scale formation, as ceramic scales are highly prone to failure by tensile stresses. On the other hand, it must not be too high either, because when high compressive stresses occur they also induce failure by cracking and buckling of the scales. In Table 2 the values of different oxides on pure metals are shown.

Oxide	MgO	Al_2O_3	ZrO_2	NiO	TiO_2	CoO	Cr_2O_3	Ta_2O_5	Nb_2O_5
PBR	0.81	1.28	1.56	1.65	1.75	1.86	2.07	2.5	2.68

Table 2. Pilling-Bedworth Ratio of different oxides on pure metals [18]

It should be noted that the PBRs of alloys are not the same as those of pure metals, so for example the PBR of an alumina scale growing on intermetallics from the Ni-Al system is significantly different to the PBR of pure Al (Table 3). So the alloy system on which an oxide grows at high temperature must be considered as well.

α-Al2O3 on	Ni_3Al	NiAl	$NiAl_3$
PBR	1.71-1.88	1.64-1.78	1.48-1.57

Table 3. Pilling-Bedworth Ratio of α-Al_2O_3 on different intermetallic aluminides [19]

After formation of the scales, the occurring stresses are dominated by the mismatch in the thermal expansion coefficients between the ceramic scale, the coating, and the alloy beneath.

When the mismatch is too high, for example with silica scales on nickel- or cobalt-based alloys, extensive cracking occurs during cyclic exposure, providing less protection than alumina and chromia, oxides which have a higher thermal expansion coefficient closer to that of the alloys underneath [20,21]. Still, even alumina or chromia scales suffer some cracking in service, but coatings for high temperatures are designed to allow self-healing of the scales.

As already mentioned, such high-temperature coating systems can be classified as diffusion coatings or overlay coatings. Ceramic thermal barrier coatings also fall into the category of overlay coatings, but these will be covered separately.

3. Diffusion coatings

Diffusion coatings are based on the enrichment of protective metallic elements close to the surface by diffusion from a reservoir outside. As for all diffusion processes, the parameters time, temperature, and phase composition are critical. The process conditions have to be optimized for each material because the phase composition and the microstructural evolution of diffusion coatings depend highly on the substrate which is coated. Figure 6 illustrates the general idea of diffusion coatings. A reservoir with a very high concentration of the element that should be enriched is created at the surface either in the gas phase or in a solid/liquid state. Due to the concentration gradient at high temperatures, elements start to diffuse into the substrate, and elements of the alloy have a tendency to diffuse outward. Depending on which process is faster, the inward or outward diffusion process is more pronounced. In both cases these processes eventually achieve the aim of changing the composition close to the surface by enrichment with the elements from the diffusion reservoir.

Several different manufacturing methods have been developed for diffusion coatings. Figure 7 gives an overview of the most important procedures. These include pack cementation, which can be done in-pack or out-of-pack (also called above the pack, which resembles the chemical vapor deposition (CVD) processes). Other processing techniques include slurry-reaction coatings, galvanic and metal foil coatings, or a hot-dipping process in a metal melt. They all
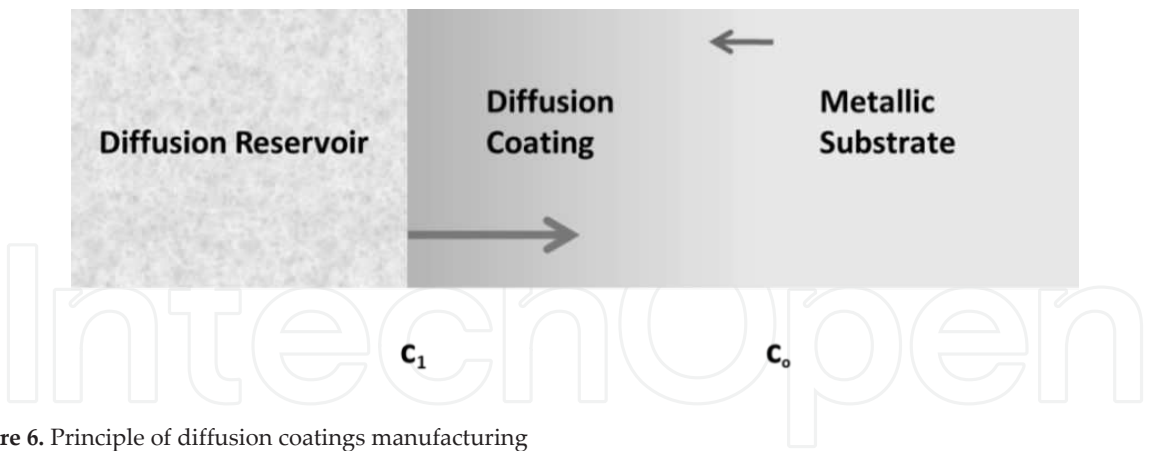
Figure 6. Principle of diffusion coatings manufacturing

have in common that a reservoir of the diffusing metal is first applied to the surface and later diffused via heat treatment.
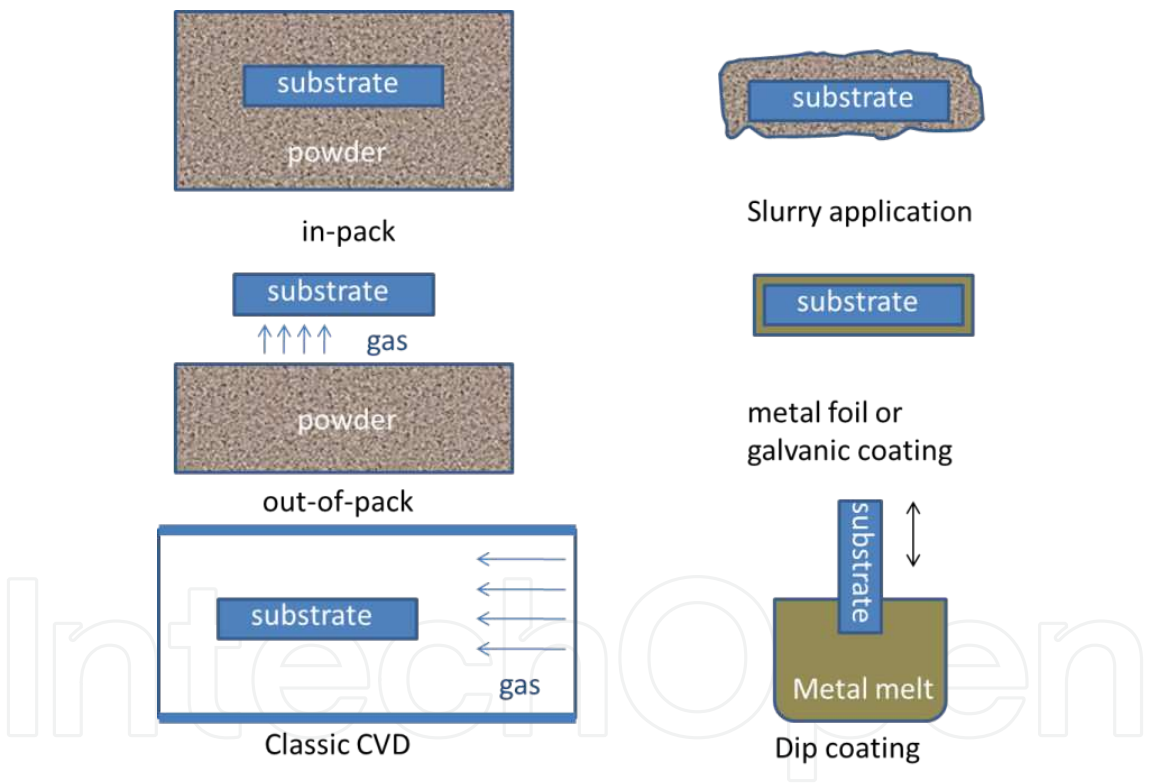

Figure 7. Different methods to produce diffusion coatings

3.1. Pack cementation processes

As early as in 1914 the first "pack cementation" process was reported by Allison and Hawkins [22]. They diffused aluminum into iron and steel, but the process did not receive much attention up to the 1950s. Since then, pack cementation with chromium has been widely used to enhance the corrosion behavior of low-alloyed steels [23]. In the 1970s, the aluminizing

process for nickel-based alloys became popular, especially in the aircraft industry. Today more than 80% of stage 1 airfoils are coated with aluminum diffusion coatings [12], most of them by the pack cementation process. It falls into the category of chemical vapor processes and is carried out at high temperatures (600-1200°C) in an inert gas atmosphere, in vacuum, or under reducing conditions. The the powder pack is composed of an inert filler (usually Al_2O_3), a halogen-carrying compound as an activator, and a metallic powder of the elements to be enriched. In the 1990s, with a better theoretical understanding of the processes, co-deposition of more than one element at a time became possible and was first developed for Al in combination with Cr [24-28] to improve the corrosion behavior when sulfur is part of the hot gas. Recently, investigations have been focusing on the modification of aluminide scales by co-diffusion with reactive elements such as Y, Ce, or Hf [29,30]. Small amounts of these elements are known to improve scale adhesion [31]. Platinum modification can also be beneficial under certain conditions since it facilitates the formation of stable alumina scales. Pt has to be galvanically applied and interdiffused before aluminum is enriched via pack cementation [32]. Silicon can also be added to the aluminide coating. Similar to chromium, it enhances the resistance against sulfur-carrying gases [33]. However, its application is usually limited to small amounts because silicon bears the risk of forming low-melting phases in nickel- or cobalt-based systems [34].

In industrial applications, the reaction is conducted in tightly sealed containers in which the components are placed. The parts can either be embedded in the reactive powder mixture ("in pack") or suspended "out-of-pack" (also called "above the pack"). In both cases either an inert or a reducing atmosphere is used. The entire container is heated to 100-200 °C to remove any residual moisture and oxygen. In the following step it is heated to the actual process temperature, which depends on the diffusing elements and on the substrates. For superalloys the temperature typically lies in the range of 900-1100°C. The holding time is dependent on the particular system and usually varies between 1 and 10 h. The optimized parameters must be evaluated for each system, usually with the help of thermodynamic calculation programs to investigate the temperature and activity of the different metal halogens which carry diffusion metals to the surface [35,36]. If the activities of the diffusing metal halides at the surface are too high, brittle phases occur frequently; if their activities are too low, too little diffusion takes place [37].

Figure 8 summarizes the major steps of the classical pack cementation process. Metal halides are formed and transported via the gas phase to the surface of the component to be coated, where the halide interacts with the sample surface and dissociates into the metal and the halogen anion. The metal atom diffuses into the substrate surface zone. The formation of the coating resembles that of diffusion couples, and the driving force for the interdiffusion is the activity or concentration gradient between the environment (which contains the diffusing elements such as Al) and the surface of the components [29]. After releasing the metal at the surface, the halogen reacts with new metal atoms from the powder to keep the process continuously alive. In any case, halogens (most common are chlorine and fluorine, but bromine or iodine can also be used) serve as an activator. The contents of activator and metallic powder determine the activity of metallic halogens and therefore the amount of metal which can react
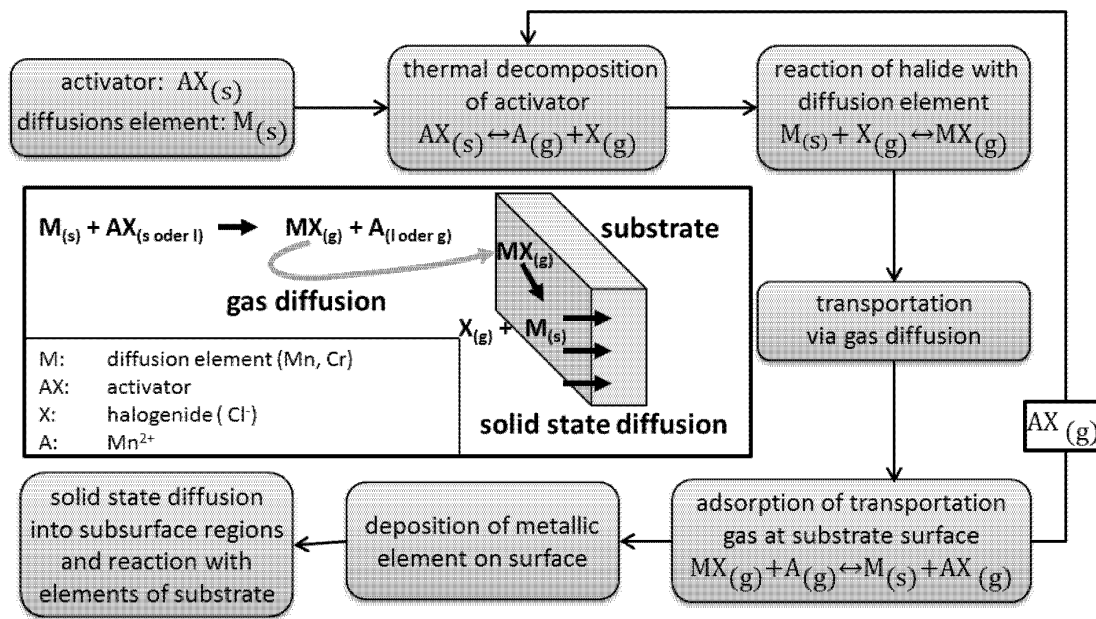
Figure 8. Major steps during the pack cementation process [38]

at the surface. The activator is added in the form of compounds such as NH_3Cl, AlF_3, or as HCl gas. The metallic powder, for example Al, can be used as pure element powder but also in an alloy form with nickel or chromium, for example CrAl powder, to lower its activity.

In any case, at the surface several intermetallic phases form according to their thermodynamic stability and local phase composition. Typical intermetallic phases that can form within the substrate metals by aluminization are $CoAl_3$, Co_2Al_5, or CoAl in cobalt-based alloys and $NiAl_3$, Ni_2Al_3, NiAl, or Ni_3Al in nickel-based alloys. As mentioned earlier, the formation of the phases at the surface is controlled by the activity (the powder composition and activator), the temperature, and the duration of the process. Goward and Boone [39] classified diffusion coatings into low- and high-activity coatings, based on observations on nickel-based alloys. A "high activity" pack structure is usually observed in pack cementation processes at lower temperatures in combination with a high aluminum activity at the surface. In this case, Ni2Al3 is formed by inward diffusion of aluminum as the dominant mechanism and the diffusion of Ni is rather low. Additionally, in aluminum-rich phases the diffusion of aluminum is favored, even in aluminum-rich NiAl. With lower Al content, its mobility decreases as well. After a high-activity process, Ni2Al3 is present at the surface, while closer to the coating–substrate interface aluminides less rich in aluminum can be found. Ni2Al3 coatings usually require a second heat treatment to transform the rather brittle phase into the desired NiAl phase. Instead, if a lower activity is used in the pack in combination with a higher temperature, Ni diffusion is faster and NiAl forms directly. As a result, these coatings grow by outward diffusion and elements of the substrate that have little solubility in the NiAl phase such as refractory metals are enriched in the substrate close to the interface as part of the so-called interdiffusion zone. In Figure 9, a high-activity coating is compared with a low-activity coating on a nickel-based superalloy.
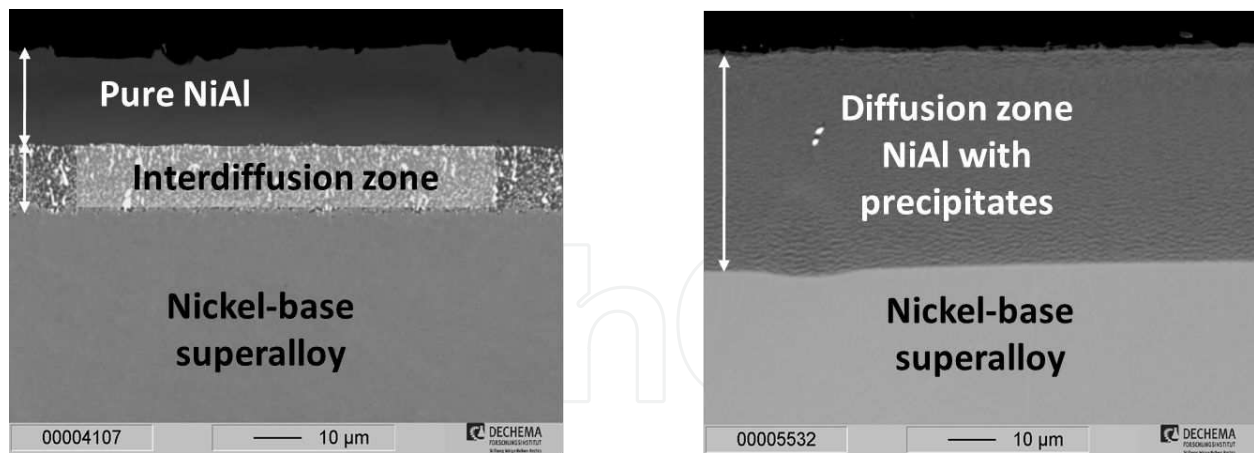
Figure 9. Comparison of a high-activity coating (left) with a low-activity coating (right) on a nickel-based superalloy substrate (PWA 1484)

Such coatings can be applied even inside of pipes. In this case, the tube is filled with the powder mixture and then sealed at the ends. The tube represents both the container and the part to be coated. This is an industrially established technique for huge components such as 15-m-long furnace tubes [40]. After the coating process, in case of "in pack," sometimes inert particles from the ceramic filler remain on the surface and must be removed. If the parts have small holes or channels, these can even be blocked by residues of the inert filler. To avoid such drawbacks, turbine blades and vanes are usually coated by using the "out of pack" technique. In all cases the huge advantage is that, since it is a gas phase process, complete coverage of the surface can be ensured.

3.2. Slurry coatings

Compared with the pack cementation process, slurry coatings were developed much later in the 1970s and 1980s [39,41]. Although the processing and formation mechanisms are totally different, they offer similar microstructure and features as coatings that were applied by pack cementation. In Figure 10, the diffusion layers obtained with these two different coating methods are shown for a nickel-based alloy (CM247). The coating on the left was produced by the pack cementation described in detail above. The other coating was achieved via the slurry aluminizing route. After 1000 h of exposure in air at 1050°C, diffusion layers of both coatings look very similar and are still protective.

Thus, the slurry route represents an interesting alternative for many systems or components, especially since slurry systems can be applied on components via common immersion, painting, or spraying methods, which is a big advantage for large parts. The slurries usually contain a metal powder, sometimes an activator, and either an organic, water-based binder or chromium-phosphate acidic binder [42,43]. Water-based activator-free systems are preferred nowadays, as the use of chromium-phosphates or halogen activators is hazardous and toxic. When the coating is applied, it also has to be heat-treated. In a first step, organic binders are burnt-out in the temperature range of 300-450°C and subsequently the metal powder reacts and diffuses into the substrate at higher temperatures between 600 and 1100°C [44]. In contrast
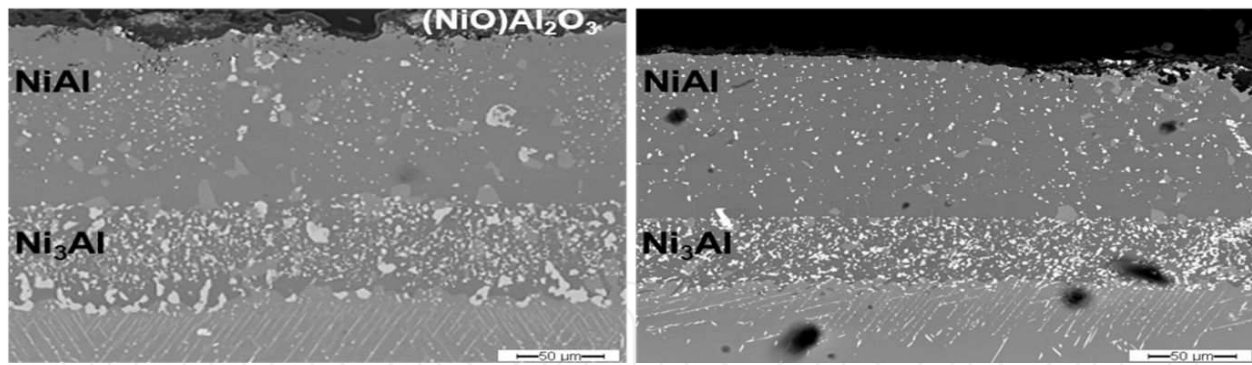
Figure 10. Diffusion coatings on a CM 247 nickel-based alloy after exposure in air at 1000°C for 1050 h. The left coating was applied by the slurry process (slurry composition: 40% Al, polyvinyl alcohol, water), the coating on the right via pack cementation (powder mixture: 5% Al, 1% NH4Cl, rest Al2O3, 1000°C, 1 h in Ar/5% H2)

to the pack cementation process no gas phase is present. Instead, above the melting point metallic melt from the metal powder wets the substrate and reacts via a combustion synthesis (exothermic formation of intermetallics) mechanism, which is extremely fast [44]. In the beginning of the process aluminum-rich phases are formed that usually require further heat-treatment so that the layers can be converted into the desired NiAl or CoAl phases (similar as for pack cementation low-activity coatings). Modification of coatings applied by this slurry technique with other elements such as chromium and silicon is also possible by alloying with aluminum particles used for the slurry or by mixing two metallic powders. Most recently, even low-activity coatings have been manufactured by the slurry technique in one step, as described in detail elsewhere [43].

Figure 7 shows an overview of application methods for diffusion coatings, including aluminum foil, galvanic or dip coatings, whose formation mechanisms can be compared to slurry coatings where a certain amount of aluminum is directly deposited on the surface and heat-treated. However, since it is much more difficult to apply homogeneous layers, such techniques are hardly used compared with the slurry technique.

4. Overlay coatings

4.1. MCrAlY-coatings

In contrast to diffusion coatings, no elements of the substrate are incorporated in overlay coatings. Therefore, such coatings offer the possibility to apply totally different compositions compared to the base materials, and their properties can be perfectly optimized to fulfill the requirements listed in Table 1, such as being corrosion-resistant as well as mechanically and thermally compatible with the substrate. Although this flexibility allows a wide range of compositions, almost all systems for superalloys are based on a general MCrAlY composition and contain usually more than four elements with M = Co or Ni or a mixture of them plus aluminum, chromium, and an element from the group of the reactive elements such as Yttrium (MCrAlY is the common term for such types of coatings and Y stands for Yttrium) [12]. One

requirement is an Al content of 10-12 wt%, which is less than in the diffusion coatings. However, a higher chromium content favors alumina formation and makes such systems reliable alumina formers. The still rather high amount of aluminum in MCrAlY coatings for superalloys forms intermetallic phases, but in this case only the β-NiAl or CoAl phase is present in the coatings. In contrast to the diffusion coatings, such phases are surrounded by a metallic nickel- or cobalt-based gamma solid solution matrix. The resulting two-phase microstructure β+γ (see Figure 11, left) increases the ductility of the coating over purely intermetallic coatings and thereby gives higher thermal fatigue resistance.
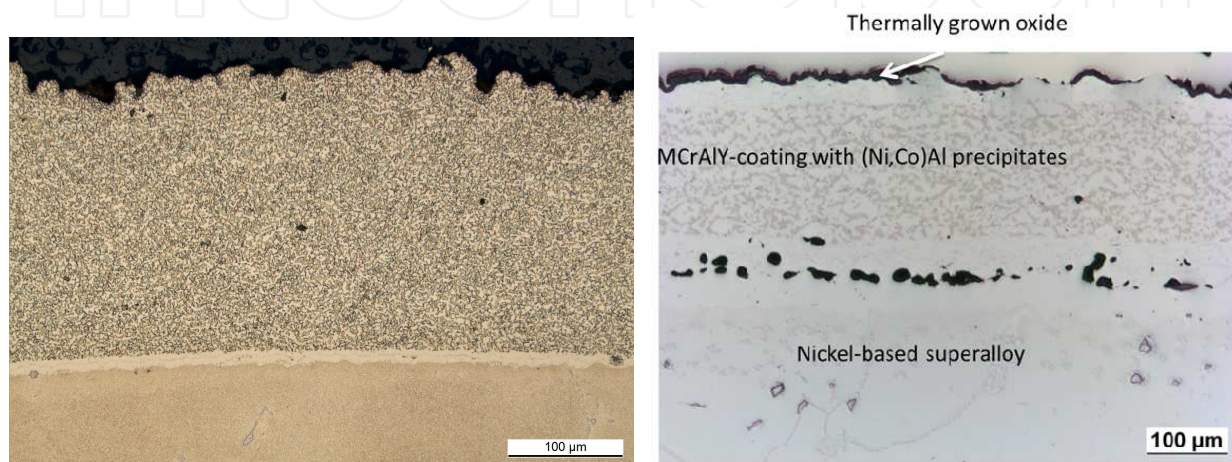

Figure 11. NiCoCrAlY coating on nickel-based superalloy; on the left a light microscopy picture after manufacturing after application [45], on the right a MCrAlY oxidized for 500 h at 1050°C in air is shown. Close to the surface the β-precipitates are dissolved and at the interface interdiffusion and interdiffusionpores (Kirkendall-pores) can be seen

One other advantage over diffusion coatings is the significant amount of Cr in the MCrAlY coatings, which enhances the corrosion and oxidation resistance. Regarding only oxidation resistance, NiCrAlY shows the best protection, but when sulfur is present in the gas, Co-based MCrAlY systems have a higher resistance. Additionally, NiCrAlY shows a phase transition above 1000°C. Therefore, usually well-balanced NiCoCrAlY or CoNiCrAlY compositions are used in industrial applications, also depending on the type of superalloy. Besides the major elements, these systems are enhanced by the addition (<1%) of reactive elements (RE) such as yttrium, cerium, lanthanum, hafnium, or zirconium. The addition of rhenium was also shown to be beneficial [46,47].

When employed at high temperatures, the coatings degrade mainly by Al depletion due to both oxide formation and interdiffusion with the substrate. The beginning of the β dissolution is already visible close to the surface and at the interface to the superalloy after 500 h at 1050°C as shown in Figure 11, right. Similar to diffusion coatings, this aluminum depletion alters the microstructure, as visible close to the surface and at the interface to the substrate. When the β-phase is totally dissolved, the coating quickly loses its protective properties. Compared to diffusion coatings, the composition and performance is optimized, but the manufacturing of overlay coatings is much more expensive. Overlay coatings are produced by one of the following processes: Physical vapor deposition (PVD) process, thermal spraying process, or

overlay welding (also called cladding). For MCrAlY overlay coatings, mainly thermal spray processes or rarely PVD processes are used.

Thermal spraying processes are a group of surface coating processes in which a spray material is partly or fully melted inside of a spray gun (electrical arc discharge is usually used as the source of energy) and accelerated toward the surface of the component to be coated in the form of micrometer-size particles. The resulting coatings are formed by the accumulation of numerous sprayed particles. Adhesion occurs primarily due to a mechanical interlocking with the surface roughness of the substrate, while metallurgical processes hardly take place and a subsequent heat treatment is required. When MCrAlY powders are sprayed in the molten state, aluminum and chromium are likely to oxidize "in-flight." Therefore, only the following three thermal spray methods are commonly used to coat superalloys with MCrAlYs: Low pressure plasma (LPPS), vacuum plasma (VPS), and high velocity oxyfuel (HVOF) spraying. Atmospheric plasma spraying (APS) is only used for the application of zirconia thermal barrier coatings for turbine blades, as discussed later. For plasma spray processes an anode and a cathode are incorporated into a spray gun producing an electric arc to ionize the operating gas. The dissociation and ionization produces heat that allows melting and spraying even refractory elements or ceramics. Several gases can be used, but typically one of the following is chosen: argon, hydrogen, helium, or their mixtures. When the powder is injected in the plasma jet, it is melted by the high temperature of the plasma torch and also propelled toward the substrate. Because of the required low pressure or inert atmosphere for MCrAlYs, the effort and cost for this process is high. High-speed processes such a high-velocity oxy-fuel spraying (HVOF) are much more efficient and have earned high industrial acceptance. By increasing the particle velocity during spraying, unwanted oxidation reactions can also be minimized without the requirement of operating in vacuum [48]. Furthermore, due to the high deformation during the solidification process in the HVOF process, very low porosities can be achieved (<1%). Another option is Physical Vapor Deposition (PVD) processes [12,49]. PVD processes are conducted in high vacuum to avoid reactions between the metal atoms and the process gas. In order to transform the coating material into the gas phase, generally two methods are employed: heating until high vapor pressures occur; or bombardment with high energetic electrons or ions to release atoms from the target. For the components of high temperature coatings, which usually have high evaporation temperatures, the second method is preferred. Various modifications of this method exist, but the electron beam heating is the most well-established one. Concentrated electron beam rays induce a high energy density on the surface of the target so that locally extremely high temperatures occur and even refractory alloys or ceramic material can be evaporated. In order to apply alloys such as MCrAlY coatings, it is important to note that the partial pressures of the different elements are very different. The composition of the melt bath or of the master alloy has to be adapted with respect to the difference in the vapor pressures during the coating process. It can be calculated, but it must be considered that they change even during the process. Especially in the beginning of the coating process, the parameters are far from equilibrium and therefore cannot produce the desired composition. For metallic alloys, different elements have to be added during the process to regulate and adapt the master alloys in a way that the manufactured coating always has the right composition. Secondly, the achieved microstructure is highly textured, with

elongated grains oriented perpendicular to the surface of the substrate. This microstructure and process is of highest technical relevance for two-component ceramic yttrium oxide-zirconium oxide layers, serving as thermal barrier top coats for superalloys.

4.2. Thermal barrier coatings

Thermal barrier coatings (TBC) are used to reduce the heat flow into the metal below in order to reduce oxidation rates and to protect it from thermal softening and accelerated creep. The main application of these systems is in stationary gas and aircraft turbines. Modern TBC systems decrease the temperature load in the superalloys beneath by 200°C, or vice versa allow an increase in operating temperature in that range to improve the turbine efficiency. TBCs consist of a combination of a bond coat which can be either a MCrAlY overlay coating or a diffusion layer with a ceramic top coat. A schematic TBC system is given in Figure 12. It shows the temperature gradient and the typical configuration on a superalloy used, e.g., as a turbine blade.
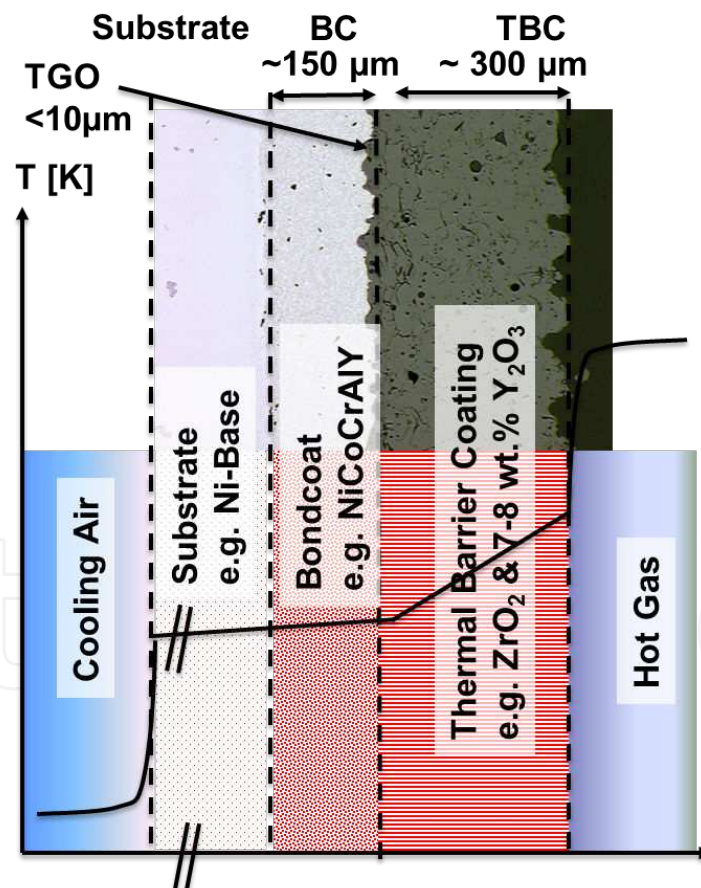

Figure 12. Different layers of a thermal barrier system and the typical temperature gradient

All classical TBC systems, which have been developed and improved throughout the last 30 years, rely on a partially stabilized zirconia as ceramic top coat, which offers a very good

combination of necessary properties [46]. Zirconia was chosen because of its low thermal conductivity in combination with a rather high thermal expansion coefficient closer to metals than that of most other ceramics [50]. In addition, it is compatible with the thermally grown alumina oxides (TGO) scales on top of the bond coat. One challenge is that ZrO is allotropic and shows three phase modifications (Figure 13).
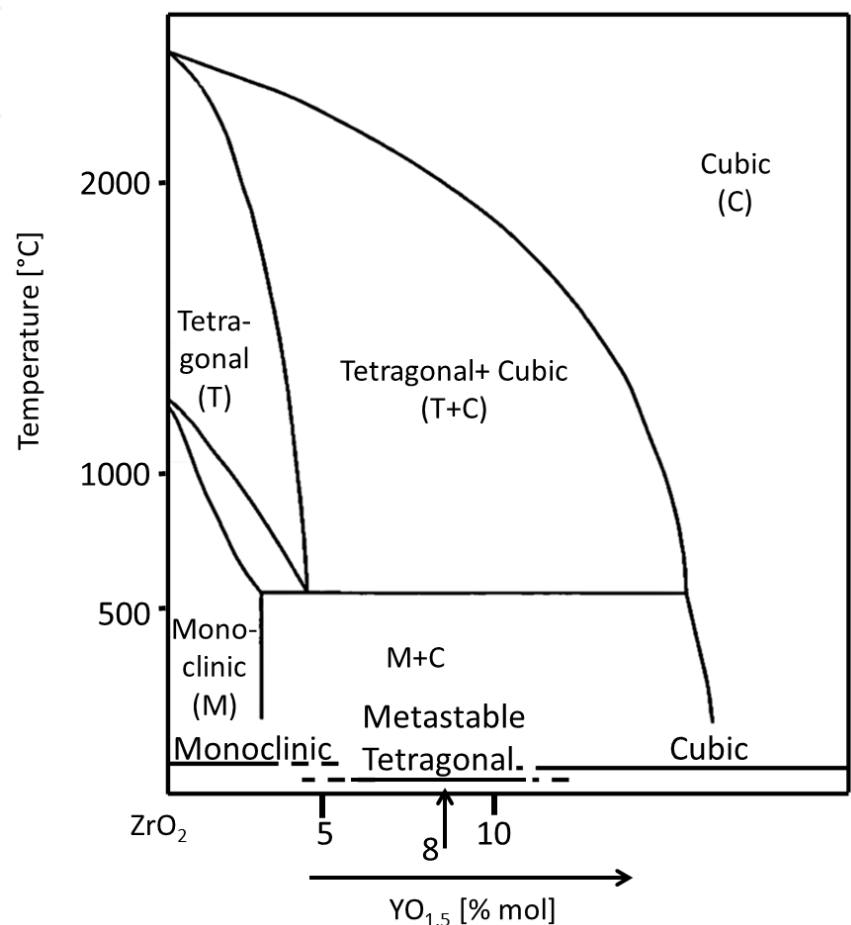

Figure 13. Phase diagram of ZrO2-Y2O3 showing the allotropy of zirconia and the technically used range in which the tetragonal lattice modification remains stable

Especially the phase transformation from tetragonal to monoclinic at about 1170°C that goes along with a volume change of about 3-9% would induce detrimental cracks. This phase transformation can be suppressed by adding oxides of Yttirum, Cer, Magnesium, Niobium, or Calcium [51]. In Figure 13, the impact of yttrium addition on the phase formation is shown. In commercial technical systems, about 8 % YO1.5 is added to receive metastable partially stabilized tetragonal zirconia and suppress detrimental phase transformations. Another modification that is technically used is MgO-stabilized zirconia, which requires about 20-25 wt.% MgO. This zirconia slowly destabilizes above about 1000°C and can only be used for components of diesel engines and not in turbines. Any phase destabilization or an increased sintering behavior at higher temperatures determines the upper temperature limit of the

application of zirconia, because it destroys the necessary porous structure and induces cracks. Such limitations trigger the investigation of other ceramics for even higher-temperature applications than the systems today allow. Especially several ziconates with a low thermal conductivity are looked at, of which the most promising candidate is gadolinium zirconate. Such coatings are developed as a two-layer ceramic system with classical zirconia under the novel ceramics [52]. Due to the fact that ceramics are prone to tensile strains, the microstructure has to be designed carefully in order to allow at least a certain strain tolerance. The ceramic layers today are either manufactured via atmospheric plasma spraying (APS) or electron beam physical vapor deposition (EB-PVD). In both cases, a certain strain tolerance is achieved by adjusting the microstructure [53].
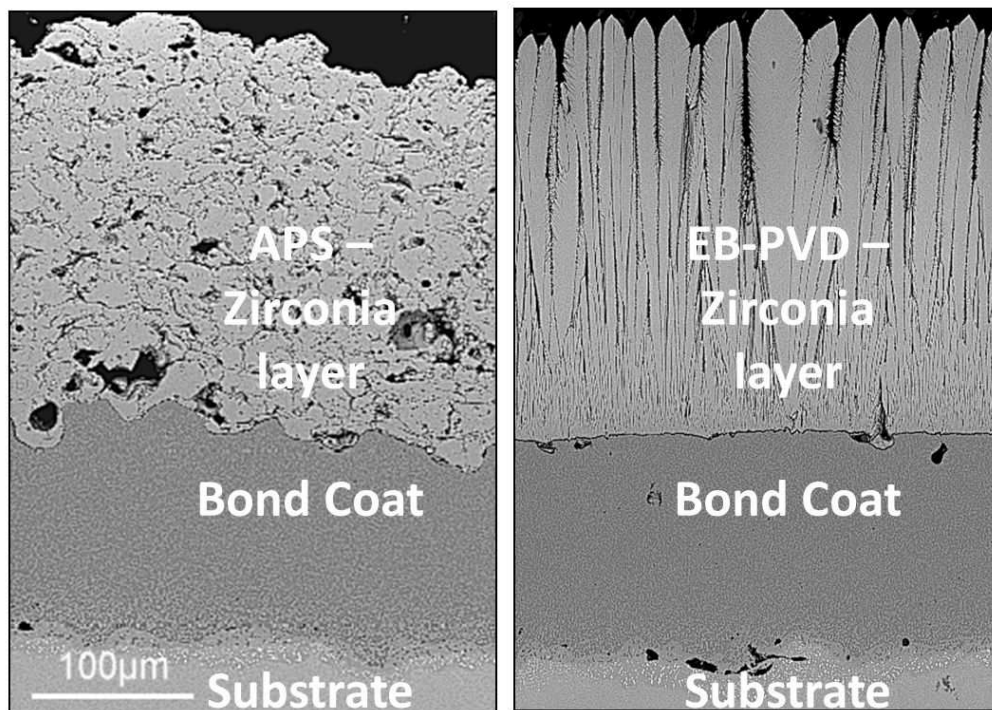

Figure 14. Comparison of TBC systems with APS-sprayed zirconia and EB-PVD zirconia top layers showing the different morphology of the ceramic coating on top of a sprayed MCrAlY bond coat on the left and a pack cemented bond coat on the right

In Figure 14, on the left the APS-sprayed microstructure is schematically shown. It possesses a pancake-like structure. The strain tolerance is created by a heavily intertwined network of fine cracks. This network separates the ceramic coating into "segmented flakes" providing a higher tolerance upon strain application through the temperature gradient or difference in thermal expansion to the material below. EB-PVD (Figure 13 on the right) coatings always exhibit the typical columnar structure. This method has the big advantage that, during the EB-PVD process, the crystals of the scales grow epitactically and perpendicular to the surface. The ceramic columns are separated from each other by small gaps, providing an exceptional tolerance to deleterious tensile strains parallel to the surface. These coatings are preferentially used for aircraft turbine blades, while for stationary turbine blades or aircraft nozzle parts

often APS coatings are employed, which can be produced at lower cost. One drawback of EB-PVD zirconia top coats is that they are sensitive to calcium-magnesia-alumina silicates (CMAS) attack [54]. CMAS can derive from the use of turbines in sandy desert areas or when volcanic ash enters a turbine. The CMAS melt in the heat chamber and are deposited on the turbine blades. When they penetrate into the TBC, they cause failure and spallation. Other factors with an influence on the lifetime are hot corrosion mechanisms by sulfur, calcium, or vanadium deposits on the coatings that can reduce the lifetime [55], often by reacting with the stabilizers (e.g., yttrium), thereby destroying the resistance against phase transformation of the zirconia. When the ceramic scale remains intact, in service an alumina scale grows slowly under the zirconia ceramic. This thermally grown oxide scale (TGO) must not exceed about 3 μm in thickness to guarantee mechanical integrity and avoid spallation [56].

5. Outlook

By using diffusion coatings, overlay coatings, and ceramic top coats for high temperatures, the otherwise often very short lifetime of unprotected materials can be enhanced and makes processes and applications possible for which otherwise no material is available. At the same time, high-temperature processes have been constantly changing due to changes in fuel or operating conditions, and the thermal operation limit of superalloys has continuously increased over the years. In the future, even systems such as molybdenum-based alloys might become interesting with a thermal application potential well above the nickel- and cobalt-based superalloys of today [9]. Such developments induce also a strong driving force to further develop high-temperature coating systems in order to keep pace with such increased operating conditions, and to allow efficient and reliable operation of metallic high-temperature materials.

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