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# Thermal barrier coatings: characteristics of microstructure and properties, generation and directions of development of bond

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### **Materials**

### **ABSTRACT**

**Purpose:** The goal of the paper is to present the review of characterisation of microstructure, properties as well as technology of receiving the heat resistance layers used as bond coats in thermal barrier coatings.

**Design/methodology/approach:** General structure characterisation of the final influence of individual TBC's sublayers was described. Especially the detailed characterisation of bond coats such as MeCrAlY and aluminides diffusion coatings was showed (used for EB-PVD obtained TBC's).

**Findings:** The influence of modification of chemical composition was described on microstructure and property of bond coats as well. It defines reactive elements such as Hf and the noble metals - Pt influence on increasing of heat resistance of bond coats, and, as a consequence, the growth of durability of coating thermal barriers. Different methods of modification of basic layers, for example the additional aluminizing process of MCrAlY coating was described as well.

**Practical implications:** Additionally, the other types of bond coats were characterised, typically used for energy conversion systems and in case of Diesel engines and especially bond coats for titanium and titanium aluminides alloys.

Originality/value: In the last part of the paper, new concepts such as "smart coatings" and diffusion barriers were shown.

Keywords: Microstructure; Titanium; Thermal barrier; Bond coat

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### 1. Introduction

From the beginning of construction of contemporary aircraft engines, in order to improve life and use properties of applied materials to maximum, the systems of protective coatings are used. Contemporary constructions of engines and development in technologies as well, lead to evolution of new protective coatings and to improvement of those which were sooner applied. The thermal barrier coatings TBC (thermal barrier coating) enable to

lower temperature (Figure 1) (at approx. 170°C) of operating elements, exposed to creeping, in a hot section of gas turbine (e.g. combustion chambers and directing and rotating blades) to a range which enables to operate for a long time in conditions of high temperature influence and prolongs operation of them even three or four times, simultaneously reducing fuel consumption [1].

The thermal barriers found application as protective layers for steel surfaces of pistons and cylinders in Diesel engines and in case of elements of compressors housing for aircraft engines, made of titanium alloys, and working surfaces of exhaust nozzles, made of niobium alloys.

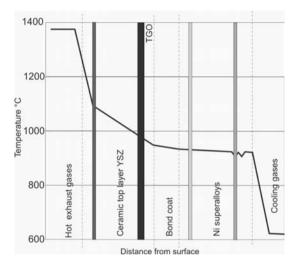


Fig. 1. Distribution of temperature on surface of an element after having applied the TBC covering [2]

# 2. General characteristics of the thermal barrier

Usually, the TBC coverings are constructed of four layers (Figure 2):

- outer ceramic zone, from which low thermal conduction is required. It is, in most cases,  $ZrO_2$  oxide stabilized with  $Y_2O_3$  (YSZ yttria stabilized cyrkonia), material of one of the lowest values of thermal conductivity in high temperature of a rank 2.3 Wm-1K-1 in  $1000^{\circ}$ C for 100% density and thermal expansion of a rank  $11\times10^{-6}{}^{\circ}$ C<sup>-1</sup>, what enables to reduce thermal stresses [3]. Usually, thickness of an outer ceramic layer is within a range  $250\text{-}375\mu\text{m}$  [4].
- bond coat of a type Ni(Co)CrAlY or diffusion layer of a type
  (Ni, Pt)Al of thickness within a range 75-125μm. A small
  value of thermal conduction, typical for ceramic materials,
  makes temperature be reduced in a zone of joint with a bond
  coat material, which is responsible for intensity of oxidation
  resistance and hot corrosion, what is an effect of high
  aluminium and chromium content. Moreover, a bond coat
  should be characterized by low susceptibility to create brittle

- phases and high resistance to diffusion of alloy components of a layer and substrate.
- layer of barrier oxides, accreting as a result of temperature growth TGO (thermally grown oxide), generated on area between an outer ceramic layer and bond coat area, as an effect of oxidation of the bond coat during oxidation and thermal shocks. Its role is to inhibit a process of oxidation of the bond coat. It is constructed mainly of the α-Al<sub>2</sub>O<sub>3</sub> oxide, which is an effect of in-core diffusion of oxygen, however it is not enough clear, if oxygen comes from atmosphere or it is an effect of disintegration of the YSZ and out-core diffusion of aluminium in temperature of operation.
- superalloys on a base of nickel, or possibly cobalt, are usually
  materials of substrate. Steel elements in Diesel engines,
  titanium alloys and alloys on a matrix of intermetallic phases
  from the Ti-Al systems and niobium alloys can also be
  applied.

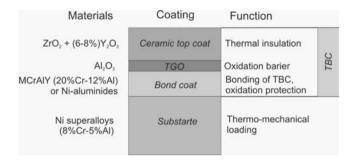


Fig. 2. Scheme of coating construction of barrier layers and a role of individual sub-layers [5]

Mostly, the TBC coverings are produced by a method of thermal spraying in the APS air atmosphere (Air Plasma Spray), at lowered pressure LPPS (Low Pressure Plasma Spray) or by the EB-PVD method (Electron Beam Physical Vapour Deposition). The barrier coatings, on elements of combustion chambers and directing blades of a turbine, are made by methods of thermal spraying with usage of plasma pistols and rotating blades are covered by means of the EB-PVD technology. Application of the EB-PVD method enabled to get a column structure, what 10-times increased life in conditions of cyclic temperature changing, comparing to the best, up to now, the TBC layers, got by a way of plasma plotting [6].

Entire characterisation of the thermal barrier coatings and mechanisms of degradation of them as well requires a detailed description of properties, microstructure and a role of individual elements, comprised in a composition of the TBC layers, especially the bond coat and ceramic outer layer. In this section it is necessary to present in details assumptions and course of internal researches to such an extent that a reader could repeat those works if he were to confirm achieved results. In short papers that information should be given as concise version as possible.

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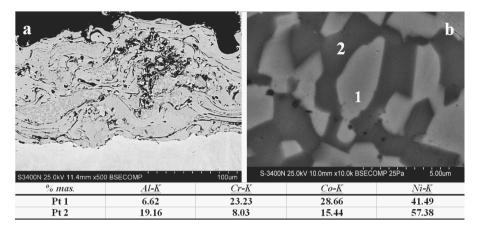


Fig. 3. Two- phase structure  $\gamma/\beta$  of layers type MCrAlY after plasma spraying [9]: a) visible two- phase areas and clusters of oxides and oxides in a banding form; b) detail from Figure 3a -two-phase area

# 3. Characteristics of bond

### 3.1. Bond coat of type MCrAIY

Oxidation resistance of the MCrAlY coverings is an effect of a compact layer formation of oxides of good adhesiveness to surface of a layer, which is a diffusion barrier and reduces speed of reaction between oxygen and chemical elements such as chromium Cr and aluminium Al. The α-Al<sub>2</sub>O<sub>3</sub> oxide is the most preferable phase component of this layer, in conditions of oxidation above 900°C [7]. Relating to it, designing chemical constitution of the MCrAlY layer is carried out in such way to provide creation of a layer of preferable oxides as a result of selective aluminium oxidation, at simultaneous consideration of satisfactory mechanical properties in conditions of cyclic temperature changing. Optimal contents of chromium is defined on a level 5-38%, aluminium adequately 8-13% and yttrium 0.5-1% (% weight), other components are nickel and/or cobalt and small amounts of reactive or noble chemical elements, however simultaneously some chemical elements recommended [8]. Minimal concentration of Al in alloys from the Ni-Al system, which is indispensable to create stable scale of aluminium oxide up to 35%, but in presence of chromium, this value decreases to 10%. A microstructure of the NiCoCrAlY covering, got in the VPS process (Vacuum Plasma Spray) is presented in Figure 3 [9].

In industrial conditions, usually the bond coats of NiCrAIY type are used for barriers, deposited by the plasma methods and NiCoCrAIY and diffusion layers of type NiAl and NiAlPt, for barriers got by the EB-PVD methods, are used as well. A difference between plasma methods and the EB-PVD method is related, first of all, with topology of surface, which is got in these processes. To create surface of high roughness and of development to get the best joint with a ceramic layer, deposited by the APS method, is required for plasma methods. In a case of settlement of a layer of zirconium oxides by the EB-PVD method, getting the surface of much higher smoothness is required, what

makes the finishing treatment or settlement of it is necessary by the EB-PVD method [10].

Influence of components, which create a layer of MCrAlY type, on properties of this layer, and thus on properties of the whole system of thermal barrier coatings, can be characterised as follows:

- nickel enables to create phases of high melting temperature, to which the  $\gamma$ ,  $\gamma$ '-Ni<sub>3</sub>Al phases are included and the  $\beta$ -NiAl phase of high oxidation resistance;
- cobalt easily substitutes nickel atoms and improves corrosion resistance in sulphur environment;
- alloys, which comprise nickel, cobalt and aluminium create the β-(Ni,Co)Al phase which shows very strong susceptibility to create a layer of oxides α-Al<sub>2</sub>O<sub>3</sub> type;
- chromium provides protective oxides of Cr<sub>2</sub>O<sub>3</sub> type to create, improving this way hot corrosion resistance and the same reducing an indispensable amount of aluminium which is necessary to create the α-Al<sub>2</sub>O<sub>3</sub> oxide;
- yttrium preferentially segregates to boundary of grains the α-Al<sub>2</sub>O<sub>3</sub> phases. Phases enriched with yttrium Y, which create themselves on these areas, make so called "pinning" the small- size grains of the α-Al<sub>2</sub>O<sub>3</sub> phase, this way filling voids, which occurred in the microstructure of scale, what influences on adhesiveness of the created protective layer and slows down a process of oxygen diffusion. As an effect of it, a process creating the complex oxides and spinels on surface of distribution of the bond coat TGO, slows down as well, what reduces a state of stresses in the layer [11].

# 3.2. Modification of a bond coat type MCrAlY

A necessity to increase life and improve mechanical properties of the MCrAlY bond coat made development of modified bond coat of this type (MCrAlXY). Reactive chemical elements (RE), high-melting metals and noble metals were introduced as well [12]. Additives of reactive modifiers, such as e.g. hafnium Hf, yttrium Y, caesium Ce, enables to increase

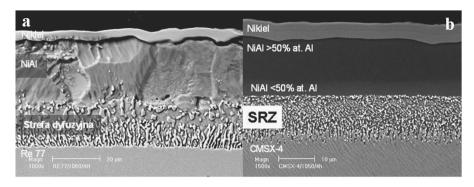


Fig. 4. Microstructure of aluminiate layer on nickel superalloy: a) diffusion transient zone and b) SRZ [9]

adhesiveness of a creating layer of the TGO oxides. A content of a modifier is comprised within a range 0.05% to 1% mass and its positive influence is visible especially in cyclic conditions of temperature changes. The noticed improvement in adhesiveness of oxide scale can be explained by several mechanisms related to microstructural changes and/or limitation of unfavourable influence of sulphur:

- changes in morphology of grains in the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> phase [13];
- reduction of stresses during creation of scale [14];
- easier plastic flow of modified fine-grained structure [13];
- reduction in segregation of sulphur to join surface of metaloxide [15];
- reduction in amount of voids on bond coat surface metaloxide by inhibiting the coalescence of vacancies [16];
- creation of stable sulphides, what reduces segregation of them to interphase boundaries [17];
- increase in energy of interphase boundaries and this way reduction in susceptibility to segregation of sulphur, inhibiting development of voids [18].

An effective way of modification can be got by diffusive aluminizing of the MCrAlY base layer, what enables to get two-layer covering, in which an outer zone (of aluminiate), including approx. 25% weight aluminium Al, show improved oxidation resistance. However an inner area, enriched with carbides of chromium and cobalt, increases hot corrosion resistance. The received layers have gradient characteristics [9].

### 3.3. Diffusion aluminides bond coats

In 1990s, diffusion aluminides coverings were applied for the first time as ground coats for thermal barrier coatings [6, 19]. Nickel aluminides, cobalt aluminides or titanium aluminides are dominating types of diffusion layers. Layers of such a type are produced as a result of deposition on treated aluminium surface, coming from powders or gases. As an effect of in-core aluminium diffusion or out-core nickel diffusion, a layer approx. 30-50 $\mu$ m thick, constructed adequately of the  $\beta$ -NiAl and Ni<sub>2</sub>Al<sub>3</sub> phases, and this layer, during next thermal treatment, undergoes changes into the  $\beta$ -NiAl phase [20]. In a case of cobalt alloys, the  $\beta$ -CoAl

creates. The \(\beta\)-NiAl phase is a basic phase component of aluminides layers, but the  $\gamma$ '-Ni<sub>3</sub>Al phase can be present as well. In a case of a high active method, presence of the TPC  $(\mu, \sigma)$ phases, topologically compacted, is also possible and the layers type α-Cr and α-W and carbides as well. Microstructure of aluminides diffusion layers depends on temperature of a process of thermal treatment and chemical constitution of substrate alloy. including concentration of carbon. Usually, in microstructure of layers, a transient zone creates itself (diffusion zone) (Figure 4a) [9], which occur as an effect of diffusion phenomena between substrate and covering. It is a zone which is impoverished with nickel (effect of out-core diffusion of nickel) and it comprises secretions (of elongated shape), enriched with heavy chemical elements of chromium Cr type, cobalt Co and tungsten W [21]. In single crystal superalloys of the third generation nickel and higher generations, the SZR zone (Secondary Reaction Zone) creates itself, what is an effect of aluminium diffusion to substrate (Figure 4b). This zone comprises phases of TCP type in a matrix of the γ'-Ni<sub>3</sub>Al phase.

Presence of the SRZ zone leads to degradation of mechanical properties of covered elements, mostly reducing creeping resistance [22].

Diffusion coatings are mostly received in a process of diffusion aluminizing or in the composed processes Al-Cr, Al-Si, Pt-Al and Ti-Al (for titanium alloys and intermetallic phases Ti-Al). In methods of activated powders, in order to get coatings of different thickness and aluminium concentration, several forms of the process are used, which depending on activity of powder, can be divided onto highly, medium and low active. During production of aluminides coatings, in high temperature approx. 1050°C, the NiAl phases of low aluminium content (low active process) originate and in temperature approx. ok. 700°C the NiAl phases of high aluminium content (high active process) originate as well. Diffusion coverings, got by a method of activated powders, are not the best solution for blades cooled by means of excavated cooling channels, because of problems related to introduction of reactive agents inside channels and removal of powder from them after a covering process [17]. Positively better, in this case, are coverings got by following gas methods: contactless (out-of-pack) or CVD, are better.

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# 3.4. Diffusion aluminides modification of bond coat

Equally as in a case of layers of MCrAlY type, also for aluminides bond coats, to improve oxidation resistance, by increase of scale adhesiveness, is a main purpose of modification. A role of chemical elements, such as hafnium Hf, zirconium Zr and yttrium Y and mechanism of operation is analogical as for the MCrAlY alloys. Hafnium is the most effective additive, which improves oxidation resistance of aluminides layers. Introduction of approx. 0.05% hafnium made the alloy be created, which has got a scale as characteristic feature of the slowest gain and the best adhesiveness among all so called "alumina formers alloys" i.e. alloys, which generate a protective layer of oxides on the Al<sub>2</sub>O<sub>3</sub> base on their surface [23-25].

Noble metals are the second group of modifiers. Introduction of platinum Pt, which is deposited before aluminizing process by an electroplating method or PVD (thickness approx. 7 µm), makes platinum be mostly used additive and this introduction is technologically the most advanced process. Platinum, having been aluminized and thermally treated, is concentrated on surface in a form of the PtAl<sub>2</sub> phase and it occurs in solid solution of the NiAl phase. At present, this group of coverings is an industrial standard and it supersedes conventional aluminides layers from applications in conditions of high temperature oxidation, cyclic oxidation and "hot corrosion" [12]. Platinum influences on phenomena, which take place during high temperature operation of coverings related to:

- increase in adhesiveness of scale to substrate as a result of stresses in an oxide layer and mechanical "pinning" of the scale:
- decrease in susceptibility to create voids on a border of distribution substrate - scale;
- · modification of morphology of this area;
- appeasement of harmful effects related to strangeness of sulphur [26-29].

Moreover, presence of platinum increases microstructural stability of a layer by slowing down out-core diffusion processes and creating the composed oxidation products (on surface and inside the layer), which worsen adhesiveness of the oxide layer [30]. Equally as chromium, platinum reduces indispensable contents of aluminium to produce the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> oxide layers, simultaneously increasing susceptibility to selective Al oxidation. It is favourable for a phenomenon of self-curing of scale in a case of cracking and dropping off [31, 32]. Despite of it, all described phenomena improve adhesiveness of scale; however, there is no certainty and unanimity concerning influence of platinum Pt on a process of oxidation of heat-resisting layers.

# 3.5. Bond coats for stationary turbine and Diesel engines

The thermal barrier coatings are designed for Diesel engines in order to improve efficiency and reduce fuel consumption. The first type of a layer was provided to the Cummins V903 engine (beginning of 1980s), which was constructed of the NiCrAlY

bond coat of the ceramic YSZ layer of total thickness approx. 1.5 mm. The bond coats were 0.1mm thick [33].

A basic difference between requirements for gas turbines and Diesel engines results from characteristics of thermal cycles - load lasts for a second and temperature does not exceed 800°C. In this case, thermal - mechanical fatigue is not a main factor, which decides about life of applied coverings. Oxidation resistance of the bond coat has also less meaning [19, 34]. In consequence, less emphasis is laid on development of the (MCrAlY) bond coats and researches are focused on influence of thickness of ceramic layer in conventional layers on a base of zirconium oxide (so called thick TBC) and they are focused on development of new ceramic materials, especially in case of Diesel engines.

In most cases, the first sections of industrial turbines are covered with layers of MCrAlY type by the VPS method without or with ceramic layers of YSZ (APS) type. The applied method EB-PVD is connected with too high costs, but it enables to get very high quality of surface from a point of view of aerodynamics and high stress resistance. Last sections and the other structural elements of a turbine, which are exposed to oxidation processes and corrosion, are covered with layers of lower costs of production (HFOV layers, covered with chromium and painted) [19].

## 3.6. Bond coats for titanium and intermetallic based Ti-Al alloys

The first researches on increase of operation temperature of alloys from the Ti-Al system up to 800°C-900°C concerned conventional diffusion aluminides coatings, constructed of the brittle TiAl<sub>3</sub> phase and of MCrAlY coatings type. The MCrAlY coatings type are characterised by high susceptibility to reaction with the TiAl substrate, what in an effect led to diffusion layers, which comprised brittle phases e.g.: AlNi<sub>2</sub>Ti in case of the NiCrAlY coating or the AlCo<sub>2</sub>Ti coating for the CoCrAlY coating. Occurrence of the Kirkendall effect was stated [35]. However coatings on a base of the TiAl<sub>3</sub> phase showed considerable great brittle, what caused the beginning of researches on influence of modifiers on increase of continuity of the TiAl<sub>3</sub> phase [36].

Wide researches are carried out on influence of chromium and silicon on properties of aluminides bond coats, deposited on the Ti-Al alloys by diffusion and physical methods.

In a sphere of the COST 501 program, e.g. diffusion coatings made by standard aluminizing process and aluminides coatings modified with platinum Pt were tested [37]. Possibilities to modify aluminides coverings, got by a method of ionic spraying, were examined. Two-phase coatings of Al-Ti-Cr type of the γ+Ti(AlCr)<sub>2</sub> structure and of L1<sub>2</sub>+Cr<sub>2</sub>Al structure were successful to get [38]. The coatings of the Al-Ti-Cr system of chromium content 8 to 10% enable to create the protective Al<sub>2</sub>O<sub>3</sub> scale during oxidation up to do 1300°C in the air. The tests showed that a coating type - Al-21Ti-23Cr (L1<sub>2</sub>+Cr<sub>2</sub>Al) is characterised by oxidation resistance, which is comparable with the CoCrAlY and CoCrAl coatings. Profitable results were also obtained for coatings from the Al-Ti-Cr system while these coatings were modified with silver in amount 1-2%, similarly as in a case of coatings type Al-Ti-Ag. Structural stability and low resistance on sulphur action are problems of these layers [39].

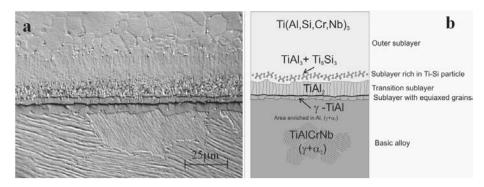


Fig. 5. a) Real microstructure and b) scheme of construction of the Ti-Al-Si coating on the TiAlCrNb alloy after homogenization in temperature 950°C [53]

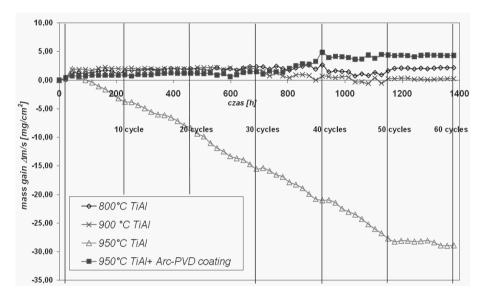


Fig. 6. Curves of cyclic oxidation of the TiAlCrNb alloy without and with the TiAlSi coating, which is got by the Arc-PVD method in temperature 950°C, 900°C and 800°C by 60 cycles [53]

Data were published on aluminides bond coats, modified with silicon as a result of application powder processes or from suspended solids e.g. these data concerned silicon - aluminizing [40,41] and as a result of application of pure silicon as protective coverings for phases from the Ti-Al system [42,43]. Tests carried out by Xiang [41] showed possibilities of simultaneous deposition of silicon and aluminium in the  $\gamma$ -TiAl alloys by a method of activated powders.

The tests were carried out on coverings of  $TiAl_3$  type, modified by silicon and got by the Arc-PVD method or by suspension method and on layers without silicon additives, deposited by the out-of-pack method of the  $(\gamma+\alpha_2)$ -TiAl alloys [44-52]. This method has many advantages, which are not attainable for powder methods - no harmful gases or ionic spraying – a coating is thicker. During deposition of it, nitrogen is not introduced, which harmfully influences on oxidation resistance and moreover, directly before deposition of the coating, clearing of alloy surface occurs. A basic advantage of the Arc-

PVD method is a possibility of simultaneous deposition of several chemical elements e.g. silicon and aluminium, what was difficult in a case of powder methods. A possibility to carry out diffusion treatment of a coating, directly after having been deposited on substrate, without a necessity to cool a covered element, is the next advantage. It enables to eliminate stresses in the coating, generated during cooling as a result of differences in coefficients of thermal expansion of the phases TiAl<sub>3</sub> and TiAl. In a final effect, the received coating is free of cracks, characteristic for coatings got by powder methods [53].

The Ti-Al-Si coating, got directly after having been deposited, was characterised by thickness approx. 30-40  $\mu$ m and was constructed of two layers of different morphology. The dominating TiAl<sub>3</sub> phase and aluminium areas and secretions, rich with silicon, titanium and chromium, create an outer layer approx. 35 $\mu$ m thick. A transition layer, approx. 5  $\mu$ m thick, created of post grains of the TiAl<sub>2</sub> phases and Ti(Al,Si)<sub>3</sub> phase created the second zone. Silicon, in amount 9% at, chromium and niobium

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were comprised in the TiAl<sub>3</sub> phase. They are chemical elements, which substitute aluminium atoms in the D022 ordered lattice, and relating to it, the phase can be described in the Ti(Al,Si,Cr,Nb)<sub>3</sub> form. An applied treatment, homogenizing in temperature 950°C, led to changes in microstructure of the Ti-Al-Si coating. The following sequence of phase occurrence in the coating was got: an outer layer constructed of the Ti(Al,Cr,Nb)<sub>3</sub> phase, in which a zone of equiaxed secretions of the Ti<sub>5</sub>Si<sub>3</sub> silicides are comprised; a transition layer constructed of the TiAl<sub>2</sub> phase; layer of equiaxed grains of the γ phase, which is an effect of enrichment of a two-phase area with aluminium; material of substrate constructed of the TiAl and Ti<sub>3</sub>Al phases [53]. Microstructure of an aluminides layer, modified with silicon, is presented on Figure 5 [48].

Presence of silicon in the coating and its influence on microstructural stability is important, especially in the first stages of growth of a transition layer. In literature, there are no data on solubility of silicon in intermetallic phases other than TiAl<sub>3</sub>. In item [54], the results concerning diffusion phenomena in the Ti-Al-Si system are presented, where it was stated that solubility of silicon Si in the TiAl<sub>2</sub> phase was approx. 4.55% at. Occurrence of the transition TiAl<sub>2</sub> layer should be accompanied by release of silicon, of which solubility in this phase is considerably lower than in a case of the TiAl<sub>3</sub> phase [54]. In a coating, directly having been deposited, presence of a transition layer, constructed of alternating post grains of silicon content 2.60% at, and 13.9%. was noticed, what corresponds to occurrence of the TiAl<sub>2</sub> phase and TiAl<sub>3</sub> phase, which is rich with silicon. Released silicon placed itself in neighbouring areas, making thus its concentration be increased almost to a limit value for the TiAl<sub>3</sub> phase. It means that further increase of the TiAl2 phase can take place only by release of silicon from the enriched Ti(Al,Si)3 phase, in a form e.g. so called the intermetallic Ti-Si compounds. It demands some energetic output and is an inhibiting factor in increase of a transition layer. Reduction in solubility of silicon leads also to create a layer, which is rich with secondary column secretions of the Ti<sub>5</sub>Si<sub>3</sub> silicides, between the outer TiAl<sub>3</sub> layer and the transition TiAl<sub>2</sub> layer. The following zones are visible there: outer zone with equiaxed secretions, then column secretions, transition zone, zone of equiaxed grains and material of substrate [53].

Heat resistance of alloy of substrate with the TiAlSi protective coating is decidedly higher than in case of basic alloy (Figure 6) [53]. The created scale has got less thickness and the Al<sub>2</sub>O<sub>3</sub> oxide is a dominating demanded component. Advantageous influence of the applied coating on improvement of heat resistance of the TiAlCrNb alloy results from presence of the TiAl<sub>3</sub> phase, which is rich with aluminium and modified with silicon. This phase is characterized by high activity of aluminium relating to titanium, what leads to a state, in which selective oxidation occurs, and the Al2O3 oxide, which is thermodynamically stable. Presence of silicon influences then on reduction of activity of titanium by creation of phases from the Ti-Si system. Modification of chemical contents of the coating with silicon enabled to create the Ti(Al,Si)<sub>3</sub> phase and Ti<sub>5</sub>Si<sub>3</sub> silicides phases of high oxidation resistance. Then, conditions, favourable for selective oxidation of aluminium originated and were also favourable to originate the protective Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> scales [53].

# 4. New conceptions of bond coats for the TBC

As it results from presented information, basic problems, related to application of diffusion conventional and modified layers concerns mainly phenomena of diffusion of aluminium and alloy chemical elements of substrate towards covering, what in effect finished the transition zones of SRZ type to be created, which have got negative influence on mechanical properties.

Application of diffusion barriers can be a solution of this problem, while a role of these barriers is to create an intermediate layer of low diffusion coefficient, what is favourable to inhibit incore diffusion of aluminium and alloy chemical elements of substrate of the layer. Several solutions were proposed e.g. application of noble metals and high-melting metals (W, Ir, Re) [56-57], intermetallic phases [58, 59] and ceramics [60]. Among others, the following layers were tested: TiN, AlN, SiC, AlON, ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Ir, Re, W. Interesting results were got for the Re-Cr layers. In this case, a diffusion layer was constructed of the  $\sigma$ -(Re,Cr,W,Ni) layer and was deposited on the TMS82+ single crystal alloy and on niobium alloy [59].

Applications of so called "smart coatings", which form functional gradient layers, are provided for operation in conditions of corrosion and high temperature oxidation. They are constructed of a base layer of MCrAlY type, and then enriched with chromium Cr and later with aluminium Al in order to get a gradient of chemical constitution. A layer, rich with aluminium, enables to protect the surface in oxidation conditions, while a layer rich with chromium increases resistance in case of phenomena of "hot corrosion" [61].

Limitation in susceptibility to so called rumpling, which vehemently decreases life of barrier layers type EB-PVD is the second matter. The tests, presented in the item [62] showed that the Ni-22Al-30Pt-Hf (%at.) alloy was characterised by susceptibility to create the Al<sub>2</sub>O<sub>3</sub> scale of good adhesiveness to substrate, simultaneously reducing tendency to "rumpling" in conditions of cyclically changeable temperature. There are grounds to say that this type of the (Ni-Al-Pt(+Hf)  $\gamma+\gamma$ ) coverings can be more effective than the  $\beta$ -NiAlPt layers, considering better creeping resistance and higher structural stability in contact with substrate – elimination of the SRZ area. Getting of such a type of coverings resolves itself into getting a layer of platinum 5-10  $\mu$ m thick and diffusion treatment, eliminating this way the aluminizing process (costs reduction) [62-65].

### **Additional information**

The paper was published also in the Archives of Materials Science.

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