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(54) **HIGH TEMPERATURE PROTECTIVE COATING**

(57) The invention relates to a high temperature protective coating based on MCrAlY coating, with M at least one element out of the group of Ni, Co and Fe, for a component of a turbo machine, especially a gas turbine, the coating containing at least at least 1.75 vol.-% chromium borides and the coating consisting of the following chemical composition (in wt.-%): 10-27 Cr; 3-12 Al; 1-4

Si; 0.1-3 Ta; 0.01-3 Y; 0.1-3 B; 0-7 M, with M being a different element out of said group compared to the remainder, and the remainder being M and inevitable impurities. A preferred embodiment is a coating with the following chemical composition: 10-27 Cr; 3-12 Al; 1-4 Si; 0.1-3 Ta; 0.01-3 Y; 0.1-3 B; 0-7 Co and the remainder being Ni and inevitable impurities.

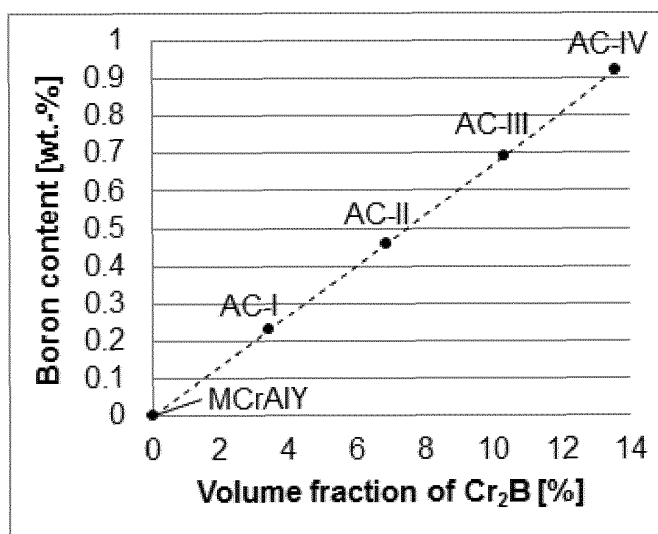


Fig. 3

Description

BACKGROUND OF THE INVENTION

[0001] The present invention relates to the technology of turbomachines, especially gas turbines. It refers to an advanced high temperature protective coating based on a MCrAlY coating (M = Ni, Co, Fe or combinations thereof) for a component of a turbomachine.

PRIOR ART

[0002] MCrAlY coatings are commonly applied on hot gas paths components of modern gas turbines. In general, MCrAlY coatings are either applied as an overlay or as a bond coat for thermal barrier coating systems (TBC).

[0003] The main target of an overlay is to protect the Ni-/Co-base superalloy substrate from oxidation and hot corrosion. Furthermore, the mechanical integrity of the coating system and of the corresponding base material shall be ensured.

[0004] During engine service, the boundary conditions (like e.g. temperature, mechanical stresses, etc.) are different for each component (per stage and even locally on the component). Some components or some specific component areas are prone to fatigue (cyclic loading), while others face increased creep, oxidation and/or hot corrosion impact (base-load).

[0005] On one hand, the modern energy market demands for industrial gas turbine (IGT)-engines running in base-load modus, on the other hand an increasing number of engines is running in (high-) cyclic modus. As a matter of fact, the mechanical and thermal loading of MCrAlY coatings used in engines running in (high-) cyclic modus differs significantly from the ones running in base-load.

[0006] Mechanical properties, like ultimate tensile strength, ductility or plastic energy, are strongly dependent on the coating composition and the related microstructure. In order to answer the requirements of modern engine operation and the related distress modes, it is of strong interest to be able to produce coatings with advanced flexibility and adjustable properties. Such a modular coating concept is for example disclosed in document EP 2 781 616 A1.

[0007] Most of the so far known MCrAlY, especially NiCrAlY coatings have been designed for answering the base load operation demand: strong oxidation and corrosion resistance. However, in (high-) cyclic operating gas turbines, the failure mode of the parts is more likely triggered by thermo-mechanic fatigue (TMF). Standard coatings usually have poor TMF resistance due to their lack of ductility at low temperatures (< 500 °C) and strength at high temperature (> 500 °C).

[0008] The lack of ductility at low temperature is caused by the large amount of fine γ' , β -(NiAl), and α -Cr precipitates (coming from the high content of Al and Cr) limiting the dislocation propagation.

[0009] The lack of strength at high temperature is caused by the partial dissolution of the γ' , β -(NiAl), and α -Cr precipitates into the γ matrix, leading to a softening effect and loss of strength.

[0010] Furthermore, when a large amount of β -(NiAl) is present this phenomenon is even increased due to the ductile to brittle transition temperature of the body centered cubic (bcc) phase.

[0011] In γ/γ' coatings, the transformation of γ' into β -(NiAl) when increasing the temperature is also an issue, as this is causing a large thermal expansion, leading to stress build-up when used as bond coat and eventually to TBC spallation. In addition, this is leading to stress accumulation in the coating (overlay) and earlier cracking. This phenomenon is limiting the maximum working temperature of the coating and/or leading to early failure in cyclic operation.

[0012] Fig. 1 shows an overview about prior art MCrAlY alloy classes and their oxidation resistance and hot corrosion resistance. This well-known figure is disclosed in: Eskner, M.: Mechanical behaviour of gas turbine coatings. Stockholm: Kungl. Tekniska högskolan., 2004, p. 3, and shows very clearly that NiCrAlY coatings have a high oxidation resistance, but as a disadvantage only a low hot corrosion resistance.

[0013] Several NiCrAlY alloys are for example described in the following documents: WO 03/060194 A1, US-A-3,620,693, US-A-4,477,538, US-A-4,537,744, US-A-3,754,903, US-A-4,013,424, US-A-4,022,587 and US-A-4,743,514.

[0014] Document WO 03/060194 A1 describes that most of NiCrAlY alloys suffer from formation of undesirable phases, like σ and/or β -(NiAl), which are detrimental if present in higher volume-fractions. Therefore, there is proposed to avoid the presence of β -(NiAl) by using a coating comprised of γ , γ' , α -Cr and a negligible content of orthorhombic M_2B (< 1 % volume fraction). The coating contains between 23 and 27 wt.% Cr, between 4 and 7 wt.% Al, between 0.1 and 3 wt.% Si, between 0.1 and 3 wt.% Ta, between 0.2 and 2 wt.% Y, between 0.001 and 0.01 wt.% B, between 0.001 and 0.01 wt.% Mg and between 0.001 and 0.01 Ca, with Ni and inevitable impurities making up the remainder. But although the formation of β -(NiAl) could be prevented, the coating still suffers from the ductile to brittle transition (DBTT) if operated at elevated temperatures.

[0015] Document US 2010/0330295 A1 describes an improvement of the coating ductility by obtaining a predominantly γ' structure that is modified with a platinum group metal in order to avoid the formation of the β -(NiAl) phase which is brittle at low temperature.

[0016] Document US 2012/0128525 A1 describes the optimization of the composition of a bond coat. The γ to γ'

transition temperature shall be increased by addition of Tantalum (preferentially without Re). Tantalum stabilizes the formation of a three phase system (β -(NiAl), γ , γ') with an increased γ/γ' transition temperature (higher than the coating service temperature), allowing reducing the local stresses.

SUMMARY OF THE INVENTION

[0017] It is an object of the present invention to provide an advanced high temperature protective MCrAlY coating for a component of a turbomachine, which coating has improved properties compared to known MCrAlY coatings, especially higher coating ductility at lower operation temperatures ($< 500^\circ\text{C}$) and significantly increased tensile strengths (at comparable strain) at elevated operation temperatures ($\geq 500^\circ\text{C}$). As a consequence, the plastic energy is increased for the entire working temperature range and crack initiation is avoided, or at least significantly reduced, leading to increased service lifetime in (high-) cyclic operation modus.

[0018] These objects are obtained by a coating according to claim 1.

[0019] The inventive advanced high temperature protective MCrAlY coating wherein M is at least one element out of the group of Ni, Co and Fe, for a component of a turbo machine, especially a gas turbine, contains at least 1.75 vol.-% chromium borides and consists of the following chemical composition (in wt.-%):

10-27 Cr; 3-12 Al; 1-4 Si; 0.1-3 Ta; 0.01-3 Y; 0.1-3 B; 0-7 M, with M being a different element out of said group compared to the remainder and the remainder being M and inevitable impurities.

[0020] According to an embodiment of the invention the coating consists of the following chemical composition (in wt.-%):

10-27 Cr; 3-12 Al; 1-4 Si; 0.1-3 Ta; 0.01-3 Y; 0.1-3 B; 0-7 Co and the remainder being Ni and inevitable impurities.

[0021] According to a further embodiment of the invention the coating consists of the following chemical composition (in wt.-%):

10-27 Cr; 3-12 Al; 1-4 Si; 0.1-3 Ta; 0.01-3 Y; 0.1-3 B; 0-7 Ni and the remainder being Co and inevitable impurities.

[0022] Preferred other embodiments of the invention are disclosed in the dependent claims.

[0023] The invention describes an advanced MCrAlYB coating class containing the element boron in higher amount. The respective material composition is disclosed as well as the application of MCrAlYB and/or Cr_2B containing coatings. Key advantages are the higher coating ductility at lower operation temperatures ($< 500^\circ\text{C}$) and significantly increased tensile strengths (at comparable strain) at elevated operation temperatures ($\geq 500^\circ\text{C}$). As a consequence, the plastic energy, toughness respectively, is increased for the entire working temperature range. Crack initiation is avoided, or at least significantly reduced, leading to increased service lifetime in (high-) cyclic operation modus. An increased ductility level is promoted at different temperatures, whereas the detrimental influence of β -(NiAl) formation and dissolution is avoided. Increased high temperature strength, ensures creep resistance in base-load operation.

[0024] The strengthening effect, resulting from the presence of CrB and/or Cr_2B precipitates, is independent of any phase transition of e.g. γ , γ' , β -(NiAl), α -Cr or σ and can easily be adjusted by the added quantity of boron. The high temperature stability of CrB and/or Cr_2B ensures a stable strengthening effect until melting of the coating matrix (e.g. γ -phase). The presence of CrB and/or Cr_2B reduces the chromium depletion rate, which is not the case for regular coatings containing only α -Cr or σ -Cr phase. In case of chromium depletion in surface near regions during operation due to oxide formation, the CrB and/or Cr_2B precipitates will progressively dissolve and release the chromium needed to form a protective chromium-oxide-scale increasing the coating service lifetime in base-load operation with respect to hot corrosion. Furthermore, the advanced coating promotes formation of highly protective alumina scales which increases the coating service lifetime in base-load operation with respect to oxidation.

[0025] The influence of the several alloying elements to the properties of the coating according to the invention is the following:

Chromium:

[0026] A sufficient Chromium (> 10 wt.-%, preferred: > 22 wt.-%) content is needed in order to form borides (Cr_2B) which deliver high temperature strength and ensure proper protection against high temperature corrosion by the formation of a protective Cr_2O_3 scale. However, the Chromium content should not exceed the upper limit of 27 wt.-% (preferred: 25 wt.-%) in order to avoid a high volume fraction of the brittle α -Cr phase present at lower temperatures, which decreases the cyclic lifetime (crack initiation due to low ductility). Furthermore, the formation of brittle carbides (type: M_6C) is

promoted by a high Chromium content. In order to avoid intense carbide formation, it is recommended that the Cr content shall not exceed the upper limit of 27 wt.-% (preferred: 25 wt.-%).

Aluminium:

[0027] In order to ensure a proper oxidation resistance (stable α -Al₂O₃ scale formation) and to reach a sufficient coating lifetime, the original Aluminium content of the coating should not be lower than 3 wt.-% (preferred: 4 wt.-%).

[0028] The formation of the brittle γ' phase (Ni₃Al), which delivers the main strengthening effect, is dependent on the Al content of the coating. For optimized mechanical properties (ductility at low temperature and strength at high temperature), the Aluminium content should be in the range of 3 - 12 wt.-% (preferred: 4 - 6 wt.-%). The Aluminium content should not exceed the upper limit of 12 wt.-% (preferred: 6 wt.-%) in order to avoid a high volume content of brittle intermetallic β -(NiAl) phase which decreases cyclic lifetime and causes large thermal expansion stresses during thermal cycling (risk of TGO/TBC spallation).

Silicon:

[0029] Silicon is acting as melting point depressant (increased ductility), promotes the formation of brittle silicates, is effective against low temperature hot corrosion and increases the oxidation resistance by increasing the activity of oxide scale formers like Al, Cr and Y. The Silicon content shall not exceed the upper limit of 4 wt.-% (preferred: 2.6 wt.-%) in order to avoid the formation of a high volume fraction of brittle silicates. For an increased oxidation resistance and optimized coating lifetime, the coating shall at least contain 1 wt.-%, preferred: 1.5 wt.-% Si.

Tantalum:

[0030] Tantalum promotes the formation of the γ' phase (increases strength), improves the oxidation resistance and is known to form carbides. In order to avoid a high volume fraction of brittle carbides, the Tantalum content shall not exceed the upper limit of 3 wt.-%. Optimized mechanical properties (with respect to tensile testing, see Fig. 4) have been found when 0.1 - 3 wt.-% (preferred: 1.5 - 3 wt.-%) of Ta are added to the alloy.

Cobalt:

[0031] This element is a solid solution strengthening element and substitutes Ni in the γ matrix and to some extent also in the γ' lattice. Furthermore, it has an influence on the γ' morphology, promotes TCP (topologically close-packed phase) formation and can decrease the high temperature corrosion resistance. The Cobalt content (in a Ni base alloy shall) not exceed the upper limit of 7 wt.-% (favoured 1 wt.-%) in order to avoid the formation of the brittle σ -phase (Co, Cr rich) which decreases the coating plasticity and cyclic lifetime respectively. Optimized properties as result of tensile testing have been found, when 0 - 1 wt.-% Cobalt are added to the alloy (favoured composition).

Yttrium:

[0032] Yttrium is added in order to increase the oxidation resistance of the coating material. Transient oxidation promotes the selective oxidation of Al and thereby a stable formation, growth and extended high temperature stability of the protective α -Al₂O₃ scale. The adherence of alumina and chromia scales on Ni and Co substrates is increased by additions of Y. Furthermore, Yttrium generally reduces the chromia oxidation rate. The Yttrium content shall not exceed the upper limit of 3 wt.-% (preferred: 1 wt.-%) in order to avoid intense formation of non-stable and inhomogeneous growing Y₂O₃ scales due to the high oxygen affinity of Yttrium. Increased oxidation resistance and a stable formation of a protective α -Al₂O₃ scale are ensured when 0.01-3 wt.-% (preferred: 0.01 - 1 wt.-%) Y are added to the alloy.

Boron:

[0033] This element is added in order to form borides (Cr₂B) which are thermodynamically stable within the entire coating operation temperature range. If less than 0.1 wt.-% Boron are added, the volume fraction of borides is too low and the strengthening effect is not present.

[0034] However, if more than 3 wt.-% (preferred: 1 wt.-%) Boron are added, a high volume fraction of brittle borides is formed and the toughness (plastic energy), cyclic lifetime respectively, decreases again.

[0035] During service, the borides (Cr₂B) act as Cr reservoir releasing Cr to the depleted γ matrix which can then diffuse towards the coating-environment-interface to form a protective Cr₂O₃ scale.

BRIEF DESCRIPTION OF THE DRAWINGS

[0036] The present invention is now to be explained more closely by means of different embodiments and with reference to the attached drawings.

Fig. 1 shows in a schematic overview MCrAlY alloy classes (according to the known prior art) and their oxidation resistance and hot corrosion resistance;

Fig. 2 shows the calculated phase fracture dependent on temperature in the range between 600 °C and 1400 °C for an advanced NiCrAlSiTaCoBY coating according to an embodiment of the invention;

Fig. 3 shows the dependence between the boron content and the Cr₂B volume fraction of the standard MCrAlY (0 wt.-% B) and 4 different advanced metallic coating systems according to embodiments of the present invention and

Fig. 4 shows tensile test results at ambient temperature (left part) and at 600 °C (right part) for common state of the art NiCrAlY coatings and for NiCrAlSiTaCoBY coatings according to several embodiments of the present invention.

DETAILED DESCRIPTION OF DIFFERENT EMBODIMENTS OF THE INVENTION

[0037] The invention describes an advanced high temperature resistant MCrAlYB coating class containing - as the main factor - the element boron, leading to the formation of chromium-borides, in higher amount (at least 1.75 vol.-% chromium-borides) compared to similar state of the art coatings. M is at least one element out of the group of Ni, Co and Fe. In addition Si and Ta are alloying elements in said MCrAlYB coating according to the invention.

[0038] Some examples of preferred embodiments are coatings consisting of the following elements (given in wt.-%), wherein the balance is always Ni and inevitable impurities:

Table 1: Chemical composition of several exemplary embodiments of the coating according to the invention

Element	Ni	Cr	Al	Si	Ta	Co	B	Y
Coating								
AC-I	Balance	24.02	5.3	2.34	1.24	1.02	0.23	0.45
AC-II	Balance	23.04	5.1	2.08	1.48	2.04	0.46	0.40
AC-III	Balance	22.07	4.9	1.82	1.72	3.06	0.69	0.35
AC-IV	Balance	21.08	4.7	1.56	1.96	4.08	0.92	0.30

[0039] The coating is applied onto the surface of a metallic component, for example a gas turbine blade made of a Ni-base superalloy.

[0040] The application is done under air, vacuum or inert gas by one of the following thermal spray processes:

- Low pressure plasma spray (LPPS)
- Vacuum plasma spray (VPS)
- Atmospheric plasma spray (APS)
- High velocity oxygen fuel (HVOF)
- Physical vapour deposition (PVD)
- Chemical vapour deposition (CVD)
- Electrochemical deposition

or by any other suited application process which is state of the art.

[0041] The coating microstructure (phase distribution), at thermodynamic equilibrium, was calculated using ThermoCalc method. The results for coating composition AC-III (see Table 1) are shown in Fig. 2. The Cr₂B volume fraction is constant over the complete test temperature range, while the α -Cr fraction is decreasing with increasing the temperature and does not more exist at temperatures above about 760 °C. In addition, the volume fraction of γ' is significantly decreasing with increasing temperature.

[0042] Fig. 3 shows the dependence between the boron content and the Cr₂B volume fraction of the standard MCrAlY (0 wt.-% B - see Table 2) and the four different advanced metallic coating systems according to the invention with their chemical composition (given in wt.-%) described in Table 1.

Table 2: Chemical composition of the tested reference standard coating

Element	Ni	Cr	Al	Si	Ta	Co	B	Y
Coating								
MCrAlY	Balance	25.0	5.5	2.6	1.0	0.5	-	0.5

[0043] The nominal content of Ni, Ta, Co, and B in the four samples of the embodiments according to the invention was increased, whereas the Cr, Al, Si and Y content was decreased. The adjustment of the coating microstructure is simple, as the volume fraction of borides is linearly increasing with the boron content.

[0044] The advanced NiCrAlSiTaCoBY coating microstructure is comprised of a γ -matrix which contains γ' , α -Cr and Cr₂B precipitates. Formation of undesirable phases like σ -Cr or β -(NiAl), which have a significant influence on the ductile to brittle temperature (DBTT) and on the coefficient of thermal expansion, is avoided. The risk of stress accumulation in the coating (overlay) leading to surface cracking and stress build-up when used as bond coat eventually causing TBC spallation is significantly reduced.

[0045] Main hardening effect for NiCrAlY alloys is precipitation hardening. With increasing temperature, the volume-fraction of γ' and α -Cr precipitates is significantly decreasing (see Fig. 2). In consequence, mechanical properties change and e.g. ultimate tensile strengths is significantly decreased. If compared to common NiCrAlY alloys, the NiCrAlSiTaCoBY coating has increased high temperature strength due to precipitation hardening by thermodynamically stable CrB and/or Cr₂B precipitates.

[0046] Tensile test results for various NiCrAlSiTaCoBY coating compositions (embodiments of the present invention) in comparison to a known state of the art NiCrAlY coating compositions (as reference material) are shown in Fig. 4.

[0047] NiCrAlSiTaCoBY coatings offer higher tensile ductility at lower temperatures and higher tensile strengths at comparable strain (< 6 %) for higher temperatures.

[0048] As a matter of fact, the disclosed advanced coating class according to the invention does perform much better in cyclic loading. Enhanced tensile strength, respectively creep resistance, at elevated temperature and less crack probability and severity due to increased ductility at low temperature do lead to a significantly extended lifetime of the high temperature protective layer.

[0049] The hot corrosion resistance will be increased, due to a diffusion-controlled dissolution of the CrB and/or Cr₂B phase which is acting as a chromium reservoir during long term service.

[0050] Boron is known to be a fast diffusing element. In case of chromium depletion in surface near regions during operation due to oxide formation, the CrB and/or Cr₂B precipitates will dissolve and progressively release chromium which is needed to form a protective chromium-oxide-scale. Furthermore, the advanced coating promotes formation of highly protective alumina scales which increases the coating service lifetime in base-load operation with respect to oxidation.

Table 3: Chemical composition of several exemplary embodiments of the coating according to the invention (in wt.-%)

Element	Ni	Cr	Al	Si	Ta	Co	B	Y
Coating								
AC-V	Balance	10.0	3.0	1.0	0.1	-	0.1	0.01
AC-VI	Balance	27.0	12.0	4.0	3.0	7.0	3.0	3.0

[0051] Coatings with a chemical composition at the lower specified range (see embodiment AC-V in Table 3) show a significant ductility, toughness respectively, increase. These coatings are especially optimized for application in high-cyclic operation with less oxidation and corrosion attack. On the other hand, coatings with a chemical composition at the upper specification range (see embodiment AC-VI, in Table 3) deliver best protection from oxidation and hot corrosion at increased ductility (compared to standard MCrAlY). These coatings are especially optimized for cyclic and base-load mode with extended service lifetime intervals (compared to the current state-of-the-art MCrAlY's).

[0052] The key advantages of the present invention are:

- High temperature protective coating with increased lifetime in (high-)cyclic operation mode and at least same lifetime in base-load modus

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- High temperature protective coating with increased ductility at low operation temperatures ($T < 500^{\circ}\text{C}$) due to an optimized microstructure with reduced volume fraction of brittle phases like $\alpha\text{-Cr}$, or γ'
- High temperature protective coating with increased tensile strength, respectively creep resistance, at higher operation temperatures ($T \geq 500^{\circ}\text{C}$) due to dispersion strengthening effect of CrB and/or Cr_2B precipitates
- High temperature protective coating with increased (w.r.t. standard MCrAlY) oxidation/hot corrosion properties due to presence of CrB and/or Cr_2B precipitates acting as chromium reservoirs in depleted areas
- Adjustable strengthening and reservoir effect due to linear relation between boron content and volume-fraction of CrB and/or Cr_2B precipitates

Claims

1. High temperature protective coating based on MCrAlY coating, with M at least one element out of the group of Ni, Co and Fe, for a component of a turbo machine, especially a gas turbine, the coating containing at least 1.75 vol.-% chromium borides and consisting of the following chemical composition (in wt.-%):

10-27 Cr;
3-12 Al;
1-4 Si;
0.1-3 Ta;
0.01-3 Y;
0.1-3 B;
0-7 M, with M being a different element out of said group compared to the remainder;

the remainder being M and inevitable impurities.

2. The coating according to claim 1, **characterized in that** the coating consists of the following chemical composition (in wt.-%):

10-27 Cr;
3-12 Al;
1-4 Si;
0.1-3 Ta;
0.01-3 Y;
0.1-3 B;
0-7 Co;

the remainder being Ni and inevitable impurities.

3. The coating according to claim 1, **characterized in that** the coating consists of the following chemical composition (in wt.-%):

10-27 Cr;
3-12 Al;
1-4 Si;
0.1-3 Ta;
0.01-3 Y;
0.1-3 B;
0-7 Ni;

the remainder being Co and inevitable impurities.

4. The coating according to one of claims 1 to 3, **characterized in that** the Cr content is 21-25 wt.-%, preferred 22-25 wt.-%.

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5. The coating according to one of claims 1 to 3, **characterized in that** the Al content is 4-6 wt.-%.
6. The coating according to one of claims 1 to 3, **characterized in that** the Si content is 1.5-2.6 Si wt.-%.
- 5 7. The coating according to one of claims 1 to 3, **characterized in that** the Ta content is 1.5-3 wt.-%.
8. The coating according to one of claims 1 to 3, **characterized in that** the Y content is 0.01-1 wt.-%.
9. The coating according to one of claims 1 to 3, **characterized in that** the B content is 0.1-1 wt.-%.
- 10 10. The coating according to one of claims 1 to 3, **characterized in that** the M content, with M being a different element out of said group compared to the remainder, is 0-1 wt.-%.

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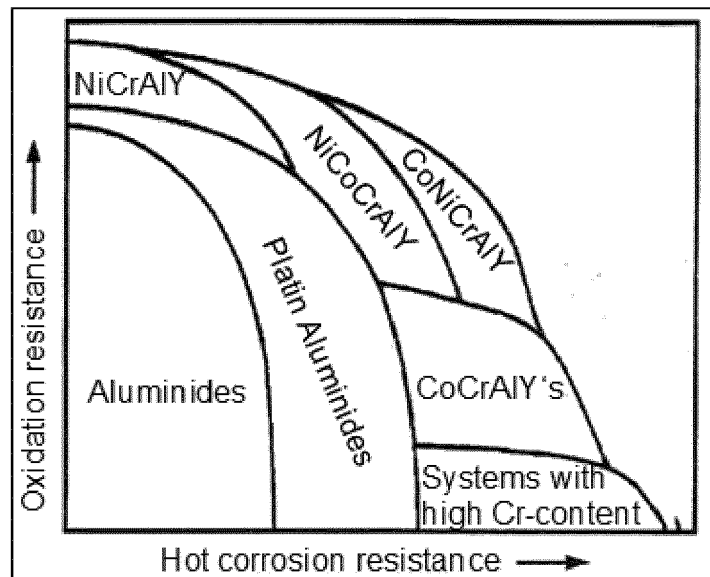


Fig. 1

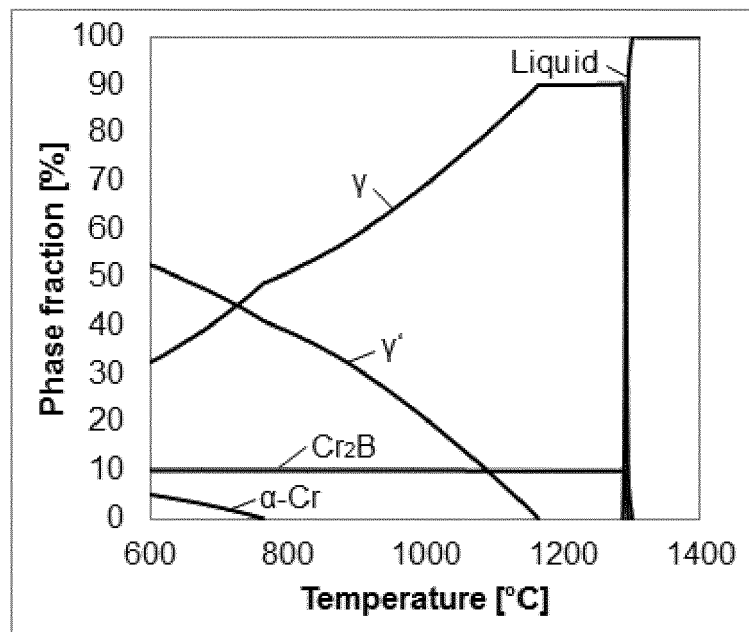


Fig. 2

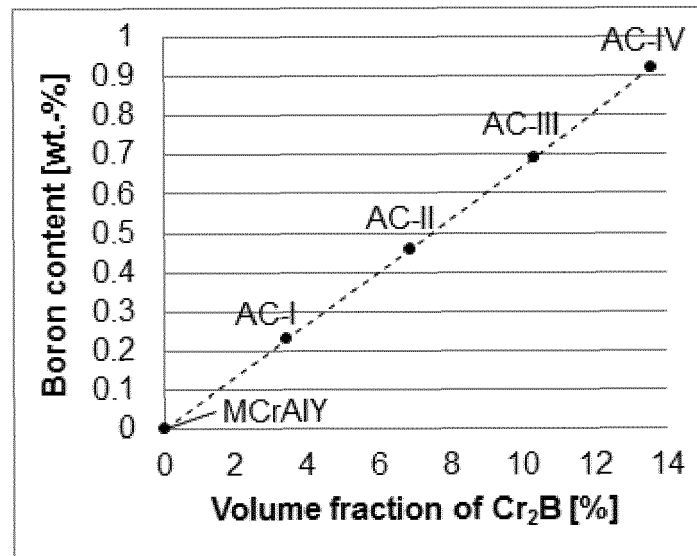


Fig. 3

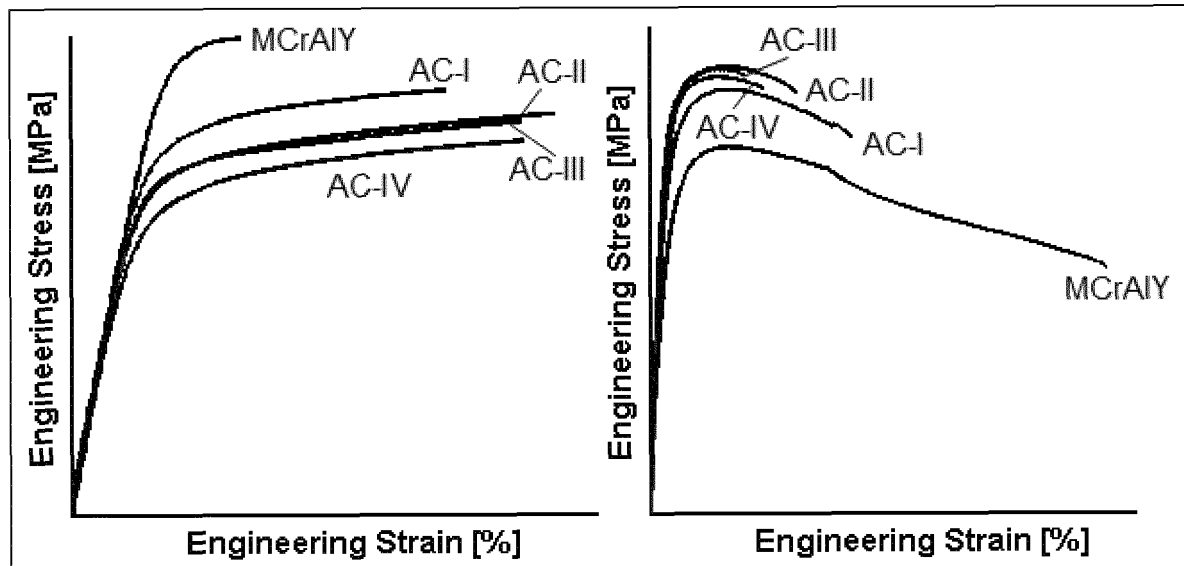


Fig. 4



EUROPEAN SEARCH REPORT

 Application Number
 EP 15 17 7229

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	US 2010/196193 A1 (MINOR MICHAEL [US]) 5 August 2010 (2010-08-05) * page 1, paragraphs 2,4,5,8-12 * * page 2; tables II,iii *	1-10	INV. C23C4/12 C23C4/08 C23C30/00 C23C4/06 C22C19/05 C22C19/07 F01D5/28
A	EP 2 374 909 A1 (UNITED TECHNOLOGIES CORP [US]) 12 October 2011 (2011-10-12) * page 2, paragraphs 2,4,5,8-12 * * page 3, paragraph 16; table II * * page 4; table III *	1-10	
A	EP 2 113 333 A2 (UNITED TECHNOLOGIES CORP [US]) 4 November 2009 (2009-11-04) * page 2, paragraphs 2,4-6,10-12 * * page 3, paragraph 13; tables I,II * * page 4, paragraphs 16,18; table III * * page 5; tables IV,V * * page 6; tables VI,VII *	1-10	
A	EP 2 248 923 A1 (SIEMENS AG [DE]) 10 November 2010 (2010-11-10) * column 7, paragraphs 41,43 * * column 8, paragraph 47 - column 9, paragraph 56 * * column 9, paragraph 58 - column 12, paragraph 77 *	1-10	TECHNICAL FIELDS SEARCHED (IPC) C23C C22C F01D
A	EP 0 194 391 A1 (GEN ELECTRIC [US]) 17 September 1986 (1986-09-17) * page 6, lines 7-13; table I * * page 7, lines 1-6,22-25; table II * * page 9, lines 4-25 *	1-10	
A	EP 2 253 738 A1 (UNITED TECHNOLOGIES CORP [US]) 24 November 2010 (2010-11-24) * page 2, paragraph 1 - page 3, paragraph 15 *	1-10	
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 23 December 2015	Examiner Joffreau, P
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1503 03.82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

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5 This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
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