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(54) Title: BURNER WITH A SLURRY COATING, WITH HIGH RESISTANCE TO METAL DUSTING

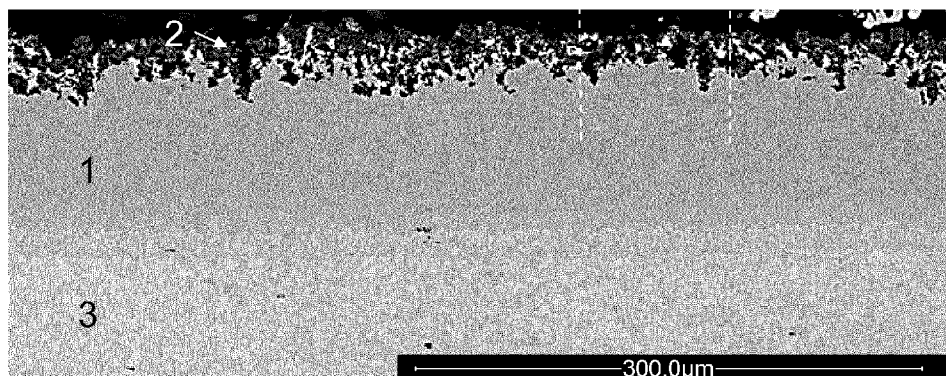


Fig. 1

(57) Abstract: At least a part of a burner for a catalytic reactor is coated with a silicate based nickel aluminide slurry diffusion coating.



Burner with a slurry coating, with high resistance to metal dusting.

The present invention is directed to combustion of hydrocarbon fuel and in particular to a burner with a slurry applied nickel aluminide diffusion coating for use in hydrocarbon fuelled combustion reactors i.e. catalytic reactors.

5 Burners of a combustion reactant are mainly used for firing gas-fuelled industrial furnaces and process heaters, which require a stable flame with high combustion intensities. Conventionally designed burners include an outer burner tube with a central burner tube for fuel supply surrounded by an oxidiser supply port. Intensive mixing of fuel and oxidiser in a combustion zone is achieved by passing the oxidiser through a swirler installed at the burner face on the central burner tube. The stream of oxidiser is, thereby, given a swirling-flow, which provides a high degree of internal and external recirculation of combustion products and high combustion intensity.

As a general drawback of conventional swirling-flow burners of the above design, the burner face is at high gas flow velocities, as required for industrial burners of this design, exposed to overheating caused by the high degree of internal recirculation along the central axis of the combustion zone. Hot combustion products thereby flow back towards the burner face, which results in rapid heating up to high temperatures and, consequently, degradation of the face due to the larger aggressiveness of the recirculating gas.

A swirling burner for use in small and medium scale applications with substantially reduced internal recirculation of combustion products toward the burner face is disclosed in US patent No. 5,496,170. The burner design disclosed in this patent results in a stable flame with high combustion intensity and without detrimental internal recirculation of hot combustion products by providing the burner with a swirling-flow of oxidiser having an overall flow direction concentrated along the axis of the combustion zone and at the same time directing the fuel gas flow towards the same axis. The disclosed swirling-flow burner comprises a burner tube and a central oxidiser supply tube concentric with and spaced from the burner tube, thereby defining an annular fuel gas channel between the tubes, the oxidiser supply tube and the fuel gas channel having separate inlet ends and separate outlet ends. U-shaped oxidiser and fuel gas injectors are arranged coaxial at the burner face. The burner is further equipped with a bluff body with static swirler blades extending inside the oxidiser injector. The swirler blades are mounted on the bluff body between their upstream end and their downstream end and extend to the surface of the oxidiser injection chamber.

US2002086257 discloses a swirling-flow burner with a burner tube comprising a central oxidiser supply tube and an outer concentric fuel supply tube, the oxidiser supply tube being provided with a concentric cylindrical guide body having static swirler blades and a central concentric cylindrical bore, the swirler blades extending from outer surface of the guide body to inner surface of oxidiser supply tube being concentrically arranged within space between the

guide body and inner wall at lower portion of the oxidiser supply tube.

Despite the above mentioned attempts to overcome the
5 problem of degradation of the burner, the burners of the known art design have been known to be challenged in cases where the operating conditions are particularly difficult. The problems experienced in those cases has been degradation of the oxidant nozzle edge of the tube. To
10 address these problems, known art suggests the use of a variety of coatings.

Accordingly, US6284324 discloses method for protecting a synthesis gas generator burner heat shield by coating the
15 burner heat shield with an overlay alloy coating composition of the formula MCrAlY wherein M is selected from the group consisting of iron, nickel, and cobalt. In a preferred embodiment, the coating includes from about 20-40 weight percent Co, 5-35 weight percent Cr, 5-10 weight
20 percent Ta, 0.8-10 weight percent Al, 0.5-0.8 Y, 1-5 weight percent Si and 5-15 weight percent Al₂O₃.

In US2010285415 a burner element is provided. The burner element includes a surface that potentially comes into
25 contact with a fuel. The surface potentially coming into contact with the fuel has a coating including aluminum oxide. A burner including the burner element is also provided. Further, a method for coating a surface of a burner element potentially coming into contact with a fuel
30 is described, wherein the surface potentially coming into contact with the fuel is coated with aluminum oxide. According to the invention described in WO09095144, a

ceramic layer is to be applied on the metal surface of a burner part facing the flame side of a burner for a gasification reactor that is fuelled with solid or liquid fuel, wherein special embodiments relate to the application of even a plurality of ceramic layers by means of the application technique of plasma spraying, particularly the materials zirconium/yttrium oxide. The service life of the burner is increased by the described coating of the burner cooling parts. Thus the availability of the system is increased while at the same time minimizing the maintenance effort. Additionally, less expensive metal materials can be used. Due to a higher permissible temperature of the supplied oxidizing agent, an increase in efficiency of the gasification process is possible.

In DE102005046198, a burner for an industrial oven or furnace has a first feed pipe for fuel gas and a second feed pipe for oxygen. Parts of the burner head are fabricated of cobalt-based alloy with an aluminum coating. Further claimed is a process to fabricate the burner head in which the cobalt/alloy components are annealed, forming an aluminum-rich surface layer.

Despite the solutions disclosed in the above mentioned known art a need still exists to provide protection to Ni-based alloys when these are subject to high temperature corrosion caused by metal dusting as is the case for burners for combustion of hydrocarbon fuel in hydrocarbon fuelled combustion reactors.

Thus, the main object of the invention is to obtain an increased resistance against high temperature corrosion

caused by metal dusting, advantageously for use in burners made of Ni base alloys which overcome the mentioned problems.

5 Accordingly, this invention is a burner with a coating on at least a part of the burner, where the coating is a nickel aluminide diffusion coating applied by a Cr (VI) free, silicate based aluminium slurry.

10 The coating may provide a significant increase in lifetime of the equipment. In some examples an increase of lifetime of the component from 2 months to more than 2 years has been observed.

15 In an embodiment of the invention the Ni base burner for a catalytic reactor comprises at least two concentric burner tubes for oxidizer and fuel supply. According to this embodiment of the invention, at least a part of one or both the burner tubes is coated with an aluminide slurry
20 diffusion coating. Although the invention advantageously is for use in large-scale burners with relative large burner tube diameters, the invention is not restricted to these large diameters, since an advantage of the invention is that the slurry diffusion coating may be applied inside
25 relative small diameter burner tubes.

In a further embodiment of the invention, the nickel aluminide slurry diffusion coating has a thickness of 10 - 1000 μm . Phase stability depends on coating thickness and
30 exposed temperature. In a further embodiment the coating thickness is at least 100 μm . The burner tubes are in a further embodiment of the invention made of a Ni-based

alloy. The invention is well suited for substrates with Ni-based alloys, as one of the advantages of the coating is that the interdiffusion of Ni in the coating and Al in the coated part of the burner is slower and to a much lower extent than the disclosed known art coatings.

The burner is in a further embodiment coated with a silicate based nickel aluminide slurry diffusion coating by applying a 10 - 1000 µm thick silicate based Al containing slurry on at least one of the burner tubes or at least a part of the burner tube(s). The application of the slurry can be done by means of spraying, brushing or immersion. Further the coating must be done by a subsequent heat treatment of the applied silicate based Al containing slurry. The heat treatment may be performed in an oven where the coated burner parts are heated separately, or it may be performed locally on the assembled burner, for instance in situ in the catalytic reactor. This is especially advantageous for large-scale burners.

In an embodiment of the invention, the heat treatment is performed in two steps as a diffusion heat treatment. The first heat treatment step is a ½ - 2 hour, preferably 1-hour diffusion heat treatment at 600°C - 800°C, preferably 700°C. The following second step is a 2 -11 hour, preferably 10-hour diffusion heat treatment at 900°C - 1200°C, preferably 1050°C. The two step diffusion heat treatment may in another embodiment of the invention be performed in an inert atmosphere containing 90% Argon and 10% Hydrogen. The controlled heat treatment prior to exposure to process conditions leads to formation of a uniform and protective metal coating.

In a second aspect, the invention comprises a method for production of a silicate based nickel aluminide slurry coating on a Ni-based alloy for protection against high temperature corrosion caused by metal dusting, said method comprising the steps of

- applying a 10 - 1000 μm thick silicate based Al containing slurry on a Ni-based alloy
- heat treating the Ni-based alloy with the applied silicate based Al containing slurry in a first step diffusion heat treatment for $\frac{1}{2}$ - 2 hour, preferably 1 hour at 600°C - 800°C, preferably 700°C
- heat treating the Ni-based alloy with the applied silicate based Al containing slurry in a second step diffusion heat treatment for 2 -11 hour, preferably 10 hours at 900°C - 1200°C, preferably 1050°C.

In an embodiment of this aspect of the invention, the slurry is applied on Ni-based alloy by means of slurry spray, paint brush or immersion. The Ni-based alloy may in further embodiments of the invention be a catalytic reactor burner tube.

More specifically, an aspect of the invention comprises the use of a silicate based nickel aluminide diffusion coating on a burner tube in a catalytic reactor burner in the temperature interval 400°C to 900°C, at a carbon activity higher than 1.

Summarizing, the advantages of the invention as described in the above aspects and embodiments comprise:

- the coating is produced from a water based slurry,

free of Cr(VI) free and environmentally benign.

- It can be applied to large surfaces and inside thin burner tubes.
- Interdiffusion of Ni in the coating and Al in the substrate will be slower. Continuous diffusion of Ni into the coating and of Al into the metal alloy is a known problem, but the particular composition according to the invention shows the lowest interdiffusion in the relevant temperature interval.
- The controlled heat treatment prior to exposure to process conditions leads to formation of a uniform and protective metal coating.

Features of the invention.

1. Burner for a catalytic reactor comprising at least two concentric burner tubes for oxidizer and fuel supply, wherein at least a part of at least one of said burner tubes is coated with a based nickel aluminide slurry diffusion coating.
2. Burner according to feature 1, coated with a silicate based nickel aluminide slurry diffusion coating.
3. Burner according to feature 2, wherein the silicate based nickel aluminide slurry diffusion coating has a thickness of between 10 - 1000 μm .
4. Burner according to any of the preceding features, wherein the burner tubes are made of a Ni-based alloy.
5. Burner according to feature 4, wherein the silicate

based nickel aluminide slurry diffusion coating is made by applying a 10 - 1000 μm thick silicate based Al containing slurry on at least one of the burner tubes.

- 5 6. Burner according to feature 5, wherein the 10 - 1000 μm thick silicate based Al containing slurry is applied on at least one of the burner tubes by means of slurry spray, paint brush or immersion.
- 10 7. Burner according to feature 5 or 6, wherein the silicate based nickel aluminide slurry diffusion coating is made by a heat treatment of the applied silicate based Al containing slurry.
- 15 8. Burner according to feature 9, wherein the heat treatment is a two-step diffusion heat treatment in vacuum, first step is a $\frac{1}{2}$ - 2 hour, preferably 1-hour diffusion heat treatment at 600°C - 800°C, preferably 700°C and the following second step is a 2 - 11 hour, preferably 10-hour
20 diffusion heat treatment at 900°C - 1200°C, preferably 1050°C.
- 25 9. Burner according to feature 8, wherein the heat treatment is performed in a reducing atmosphere of 80 - 100 % Argon and 0 - 20% Hydrogen.
- 30 10. Method for production of a silicate based nickel aluminide slurry coating on a Ni-based alloy of a burner for protection against high temperature corrosion caused by metal dusting, said method comprising the steps of
- applying a 10 - 1000 μm thick silicate based Al containing slurry on the Ni-based alloy

- heat treating the Ni-based alloy with the applied silicate based Al containing slurry in a first step diffusion heat treatment in vacuum for $\frac{1}{2}$ - 2 hour, preferably 1 hour at 600°C - 800°C, preferably 700°C
- 5 • heat treating the Ni-based alloy with the applied silicate based Al containing slurry in a second step diffusion heat treatment in vacuum for 2 - 11 hour, preferably 10-hour at 900°C - 1200°C, preferably 1050°C.

10

11. Method according to feature 10, wherein the slurry is applied on Ni-based alloy of a burner by means of slurry spray, paint brush or immersion.

15 12. Method according to feature 10 or 11, wherein said Ni-based alloy is a catalytic reactor burner tube.

13. Use of a silicate based nickel aluminide diffusion coating on a burner tube in a catalytic reactor burner in
20 the temperature interval 400°C to 900°C, at a carbon activity higher than 1.

Position numbers

- 25 01. Coating
02. Coating surface
03. Ni-based alloy

Fig. 1 shows the cross section of a sample after 5 weeks' metal dusting test. Position 1 is the coating, and position
30 2 is oxides formed on the coating, whereas position 3 is the base alloy. No metal dusting is detected.

Fig. 2 shows a magnification of Fig. 1. Position 1: coating, Position 2: oxides, and position 3: mounting material.

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Fig. 3 shows a magnification of Fig. 1 of the interface coating/base alloy. Position 1: coating, Position 2: base alloy.

10 Interdiffusion is measured as changes in the Ni/Al ratio in the coating, compared to the original Ni/Al ratio. With time, Ni diffuses from the base metal into the coating and Al diffuses from the coating into the base metal alloy. Depending on the diffusion rate of Ni and Al, the ratio
15 Ni/Al changes with time. If the Ni/Al increases significantly with time the resistance to metal dusting changes; experiments have shown that the coating becomes less resistant against metal dusting.

20 The best coating is considered to be the one with most constant Ni/Al with time, because it will show the slowest interdiffusion.

Fig. 3 shows that composition 4 has a high interdiffusion
25 rate compared to the other 3. Fig. 4 enlarges the scale to compare compositions 1 - 3. Composition 3 shows linear growth with time and it is therefore not as advantageous as compositions 1 and 2 which show a slight increase in the beginning, but remains stable after that. Compositions
30 close to 1 and 2 will be preferred.

Example

Metal dusting test of coated Ni-based alloy bars in the temperature range from 200 to 800 °C under very aggressive conditions with very low steam/carbon, under pressure 28.5 bar(g) for five weeks. The coating had been applied and heat treated in the range described in the invention. The thickness of the coating in the range 50 - 200 µm were tested. The coated Ni-based alloy bars did not show any metal dusting after 5 weeks, as compared to not-coated Inconel 601 bars which show metal dusting after less than one week.

Claims

1. Burner for a catalytic reactor comprising at least two concentric burner tubes for oxidizer and fuel supply,
5 wherein at least a part of at least one of said burner tubes is coated with a based nickel aluminide slurry diffusion coating.
2. Burner according to claim 1 coated with a silicate based
10 nickel aluminide slurry diffusion coating.
3. Burner according to claim 2, wherein the silicate based nickel aluminide slurry diffusion coating has a thickness of between 10 - 1000 μm .
15
4. Burner according to any of the preceding claims, wherein the burner tubes are made of a Ni-based alloy.
5. Burner according to claim 4, wherein the silicate based
20 nickel aluminide slurry diffusion coating is made by applying a 10 - 1000 μm thick silicate based Al containing slurry on at least one of the burner tubes.
6. Burner according to claim 5, wherein the 10 - 1000 μm
25 thick silicate based Al containing slurry is applied on at least one of the burner tubes by means of slurry spray, paint brush or immersion.
7. Burner according to claim 5 or 6, wherein the silicate
30 based nickel aluminide slurry diffusion coating is made by a heat treatment of the applied silicate based Al containing slurry.

8. Burner according to claim 7, wherein the heat treatment is a two step diffusion heat treatment in vacuum, first step is a ½ - 2 hour, preferably 1-hour diffusion heat treatment at 600°C - 800°C, preferably 700°C and the following second step is a 2 - 11 hour, preferably 10 hour diffusion heat treatment at 900°C - 1200°C, preferably 1050°C.
9. Burner according to claim 8, wherein the heat treatment is performed in a reducing atmosphere of 80 - 100 % Argon and 0 - 20% Hydrogen.
10. Method for production of a silicate based nickel aluminide slurry coating on a Ni-based alloy of a burner for protection against high temperature corrosion caused by metal dusting, said method comprising the steps of
- applying a 10 - 1000 µm thick silicate based Al containing slurry on the Ni-based alloy
 - heat treating the Ni-based alloy with the applied silicate based Al containing slurry in a first step diffusion heat treatment in vacuum for ½ - 2 hour, preferably 1 hour at 600°C - 800°C, preferably 700°C
 - heat treating the Ni-based alloy with the applied silicate based Al containing slurry in a second step diffusion heat treatment in vacuum for 2 - 11 hour, preferably 10-hour at 900°C - 1200°C, preferably 1050°C.
11. Method according to claim 10, wherein the slurry is applied on Ni-based alloy of a burner by means of slurry spray, paint brush or immersion.

12. Method according to claim 10 or 11, wherein said Ni-based alloy is a catalytic reactor burner tube.

- 5 13. Use of a silicate based nickel aluminide diffusion coating on a burner tube in a catalytic reactor burner in the temperature interval 400°C to 900°C, at a carbon activity higher than 1.

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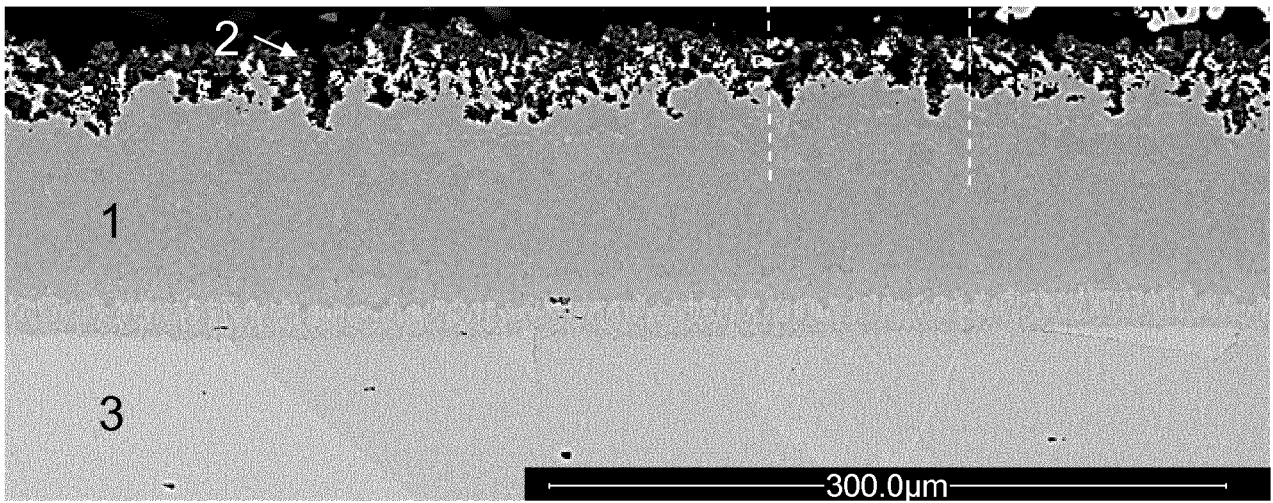


Fig. 1

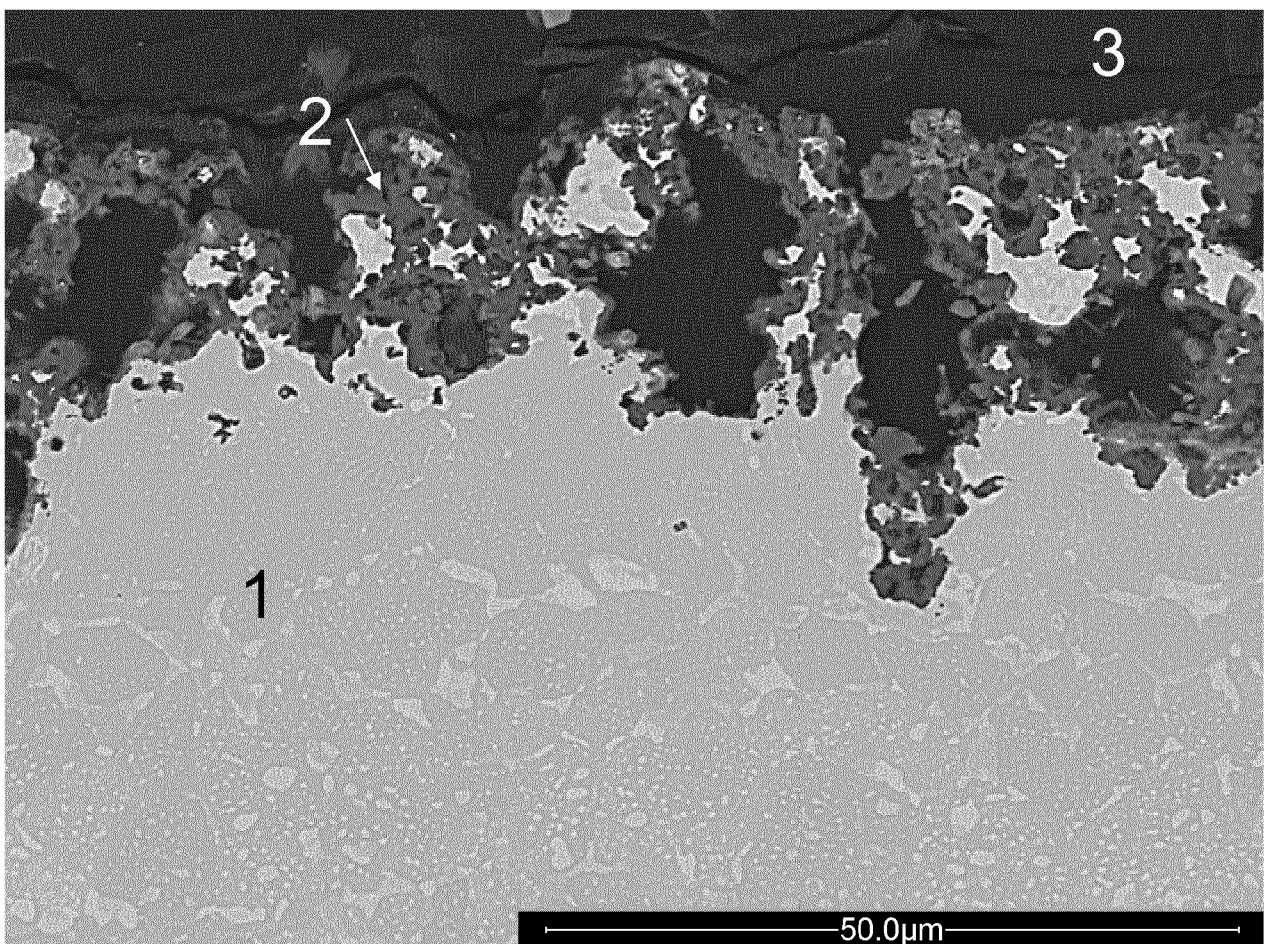
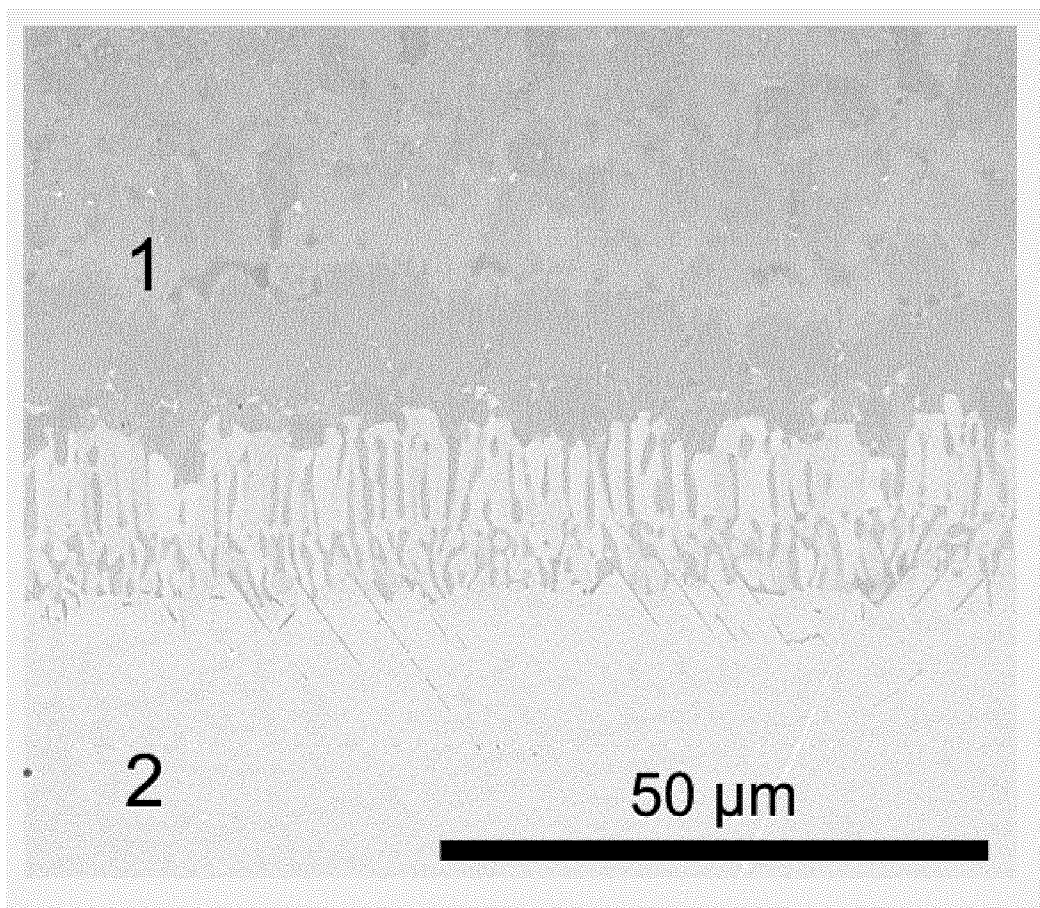


Fig. 2

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Fig. 3



3/3

Fig. 4

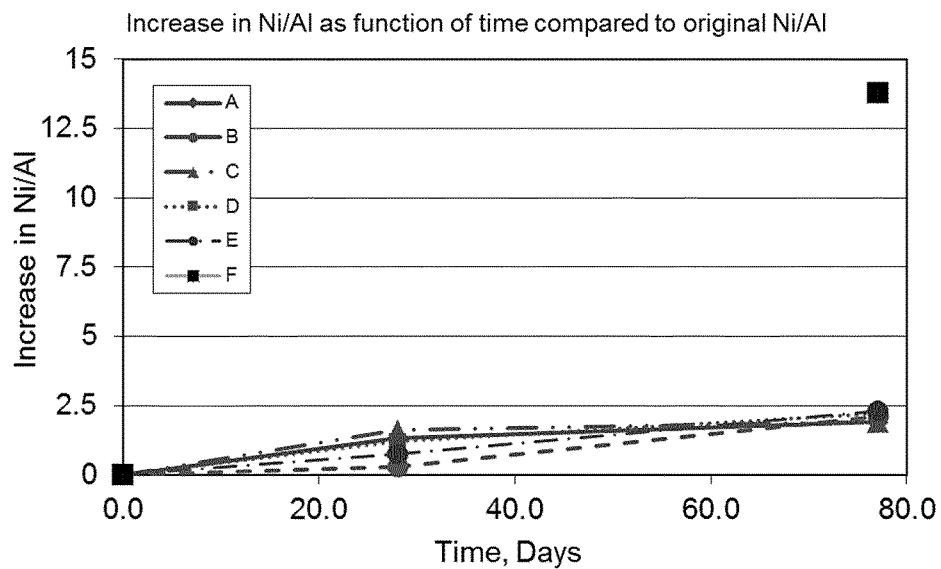
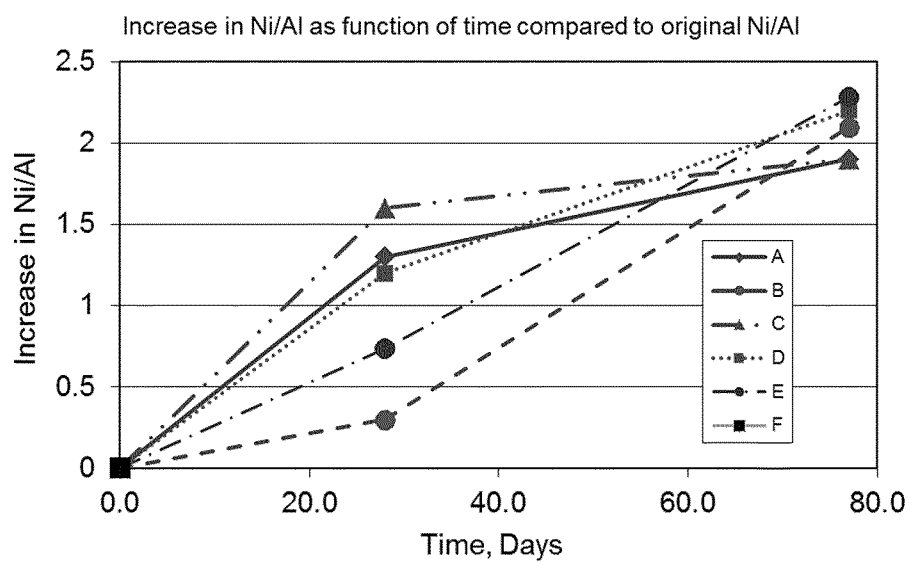


Fig. 5



INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER
INV. F23D14/22 F23D14/48 C23C10/20
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
F23D C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	WO 2016/124567 A1 (CASALE SA [CH]) 11 August 2016 (2016-08-11)	1,4
A	page 1, line 5 - page 2, line 7; figure 1 page 3, line 10 - line 12 page 5, line 25 - page 5, line 10 -----	10,13
Y	US 5 547 770 A (MEELU MEHAR C [GB] ET AL) 20 August 1996 (1996-08-20)	1,4
A	column 1, line 6 - line 15 column 1, line 32 - line 40 column 1, line 58 - column 2, line 4 column 4, line 15 - line 54 column 6, line 66 - column 8, line 14 ----- -/--	10,13



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

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Name and mailing address of the ISA/

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2018/074919

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 2 730 679 A1 (PRAXAIR TECHNOLOGY INC [US]) 14 May 2014 (2014-05-14) paragraphs [0001], [0016], [0018], [0024] paragraphs [0026], [0027]; claim 1 -----	2,5-12
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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