Title: COATING SYSTEM FOR HIGH TEMPERATURE STAINLESS STEEL

[Continued on next page]

Abstract: A method for protecting carbon steel and stainless steel, and particularly high temperature stainless steel, from coking and corrosion at elevated temperatures in corrosive environments, such as during ethylene production by pyrolysis of hydrocarbons or the reduction of oxide ores, by coating the steel with a coating of McrA1X or McrA1XT in which M is nickel, cobalt, iron or a mixture thereof, X is yttrium, hafnium, zirconium, lanthanum, scandium or combination thereof, and T is silicon, tantalum, titanium, platinum, palladium, rhenium, molybdenum, tungsten, niobium, or combination thereof. The coating and substrate preferably are heat-treated at about 1000 to 1200 °C for at least about 10 minutes, preferably about 20 minutes to 24 hours, effective to metallurgically bond the overlay coating to the substrate and to form a multiphased microstructure. The coating preferably is aluminized by depositing a layer of aluminum thereon and subjecting the resulting coating to oxidation at a temperature above about 1000 °C for a time effective to form an aluminia surface layer. An intermediary aluminum-containing interlayer may be deposited directly onto the substrate prior to deposition of the overlay coating and is heat-treated with the coating to form a protective interlayer between the stainless steel substrate and coating to disperse nitride formation at the substrate/coating interface. Also, the coating may be deposited onto and metallurgically bonded to the substrate by plasma transferred arc deposition of atomized powder of McrA1XT, obviating the need for a separate heat treatment. Alternatively, a blended powder composition to produce a desired McrA1XT alloy may be applied to the substrate.

Published: without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the “Guidance Notes on Codes and Abbreviations” appearing at the beginning of each regular issue of the PCT Gazette.
BACKGROUND OF THE INVENTION

COATING SYSTEM FOR HIGH TEMPERATURE STAINLESS STEEL

(i) **Field of the Invention**

The present invention relates to coating systems for the generation of a protective surface for carbon steel and stainless steel and, more particularly, relates to the provision of metal alloy coatings on the internal wall surfaces of high-temperature stainless steel tubes and fittings to produce a surface that provides corrosion resistance erosion resistance, and reduces the formation of catalytic coking in hydrocarbon processing such as in olefin production and in direct reduction of ores. The protective system also has application on carbon steels. For example, in downhole oil and gas applications, the protective system enhance erosion and corrosion properties compared to carbon steel commonly used.

(ii) **Description of the Related Art**

Stainless steels are a group of alloys based on iron, nickel and chromium as the major constituents, with additives that can include carbon, tungsten, niobium, titanium, molybdenum, manganese, and silicon to achieve specific structures and properties. The major types are known as martensitic, ferritic, duplex and austenitic steels. Austenitic stainless steel generally is used where both high strength and high corrosion resistance is required. One group of such steels is known collectively as high temperature alloys (HTAs) and is used in industrial processes that operate at elevated temperatures generally above 650°C and extending to the temperature limits of ferrous metallurgy at about 1150°C. The major austenitic alloys used have a composition of iron, nickel or chromium in the range of 18 to 42 wt.% chromium, 18 to 48 wt.% nickel, balance iron and other alloying additives. Typically, high chromium stainless steels have about 31 to 38 wt% chromium and low chromium stainless steels have about 20 to 25 wt% chromium.

The bulk composition of HTAs is engineered towards physical properties such as creep resistance and strength, and chemical properties of the surface such as corrosion
resistance. Corrosion takes many forms depending on the operating environment and includes carburization, oxidation and sulfidation. Protection of the bulk alloy is often provided by the surface being enriched in chromium oxide (chromia). The specific compositions of the alloys used represent an optimization of physical properties (bulk) and chemical properties (surface). The ability of addressing the chemical properties of the surface through a surface alloy, and physical properties through the bulk composition, would provide great opportunities for improving materials performance in many severe service industrial environments.

Surface alloying can be carried out using a variety of coating processes to deliver the right combination of materials to the component's surface at an appropriate rate. These materials would need to be alloyed with the bulk matrix in a controlled manner that results in a microstructure capable of providing the pre-engineered or desired benefits. This would require control of the relative interdiffusion of all constituents and the overall phase evolution. Once formed, the surface alloy can be activated and reactivated, as required, by a reactive gas thermal treatment. Since both the surface alloying and the surface activation require considerable mobility of atomic constituents at temperatures greater than 700°C, HTA products can benefit most from the procedure due to their designed ability of operating at elevated temperatures. The procedure can also be used on products designed for lower operating temperatures, but may require a post heat treatment after surface alloying and activation to reestablish physical properties.

Surface alloys or coating systems can be engineered to provide a full range of benefits to the end user, starting with a commercial base alloy chemical composition and tailoring the coating system to meet specific performance requirements. Some of the properties that can be engineered into such systems include: superior hot gas corrosion resistance (carburization, oxidation, sulfidation); controlled catalytic activity; and hot erosion resistance.

Two metal oxides are mainly used to protect alloys at high temperatures, namely chromia and alumina, or a mixture of the two. The compositions of stainless steels for high temperature use are tailored to provide a balance between good mechanical properties and good resistance to oxidation and corrosion. Alloy compositions which can provide an alumina scale are favoured when good oxidation resistance is required,
whereas compositions capable of forming a chromia scale are selected for resistance to hot corrosive conditions. Unfortunately, the addition of high levels of aluminum and chromium to the bulk alloy is not compatible with retaining good mechanical properties and coatings containing aluminum and/or chromium normally are applied onto the bulk alloy to provide the desired surface oxide.

One of the most severe industrial processes from a materials perspective is the manufacture of olefins such as ethylene by hydrocarbon steam pyrolysis (cracking). Hydrocarbon feedstock such as ethane, propane, butane or naphtha is mixed with steam and passed through a furnace coil made from welded tubes and fittings. The coil is heated on the outer wall and the heat is conducted to the innerwall surface leading to the pyrolysis of the hydrocarbon feed to produce the desired product mix at temperatures in the range of 850 to 1150°C. An undesirable side effect of the process is the buildup of coke (carbon) on the innerwall surface of the coil. There are two major types of coke: catalytic coke (or filamentous coke) that grows in long threads when promoted by a catalyst such as nickel or iron, and amorphous coke that forms in the gas phase and plates out from the gas stream. In light feedstock cracking, catalytic coke can account for 80 to 90% of the deposit and provides a large surface area for collecting amorphous coke.

The coke can act as a thermal insulator, requiring a continuous increase in the tube outerwall temperature to maintain throughput. A point is reached when the coke buildup is so severe that the tube skin temperature cannot be raised any further and the furnace coil is taken offline to remove the coke by burning it off (decoking). The decoking operation typically lasts for 24 to 96 hours and is necessary once every 10 to 90 days for light feedstock furnaces and considerably longer for heavy feedstock operations. During a decoeke period, there is no marketable production which represents a major economic loss. Additionally, the decoeke process degrades tubes at an accelerated rate, leading to a shortened lifetime. In addition to inefficiencies introduced to the operation, the formation of coke also leads to accelerated carburization, other forms of corrosion, and erosion of the tube innerwall. The carburization results from the diffusion of carbon into the steel forming brittle carbide phases. This process leads to volume expansion and the embrittlement results in loss of strength and possible crack initiation. With increasing carburization, the alloy’s ability of providing some coking resistance through the
formation of a chromium based scale deteriorates. At normal operating temperatures, half of the wall thickness of some steel tube alloys can be carburized in as little as two years of service. Typical tube lifetimes range from 3 to 6 years.

It has been demonstrated that aluminized steels, silica coated steels, and steel surfaces enriched in manganese oxides or chromium oxides are beneficial in reducing catalytic coke formation. Alonizing™, or aluminizing, involves the diffusion of aluminum into the alloy surface by pack cementation, a chemical vapour deposition technique. The coating provides an alumina scale which is effective in reducing catalytic coke formation and protecting from oxidation and other forms of corrosion. The coating is not stable at temperatures such as those used in ethylene furnaces, and also is brittle, exhibiting a tendency to spall or diffuse into the base alloy matrix. Generally, pack cementation is limited to the deposition of one or two elements, the co-deposition of multiple elements being extremely difficult. Commercially, it is generally limited to the deposition of only a few elements, mainly aluminum. Some work has been carried out on the codeposition of two elements, for example chromium and silicon. Another approach to the application of aluminum diffusion coatings to an alloy substrate is disclosed in U. S. Patent 5,403,629 issued to P. Adam et al. This patent details a process for the vapour deposition of a metallic interlayer on the surface of a metal component, for example by sputtering. An aluminum diffusion coating is thereafter deposited on the interlayer.

Alternative diffusion coatings have also been explored. In an article in "Processing and Properties" entitled "The Effect of Time at Temperature on Silicon-Titanium Diffusion Coating on IN738 Base Alloy" by M. C. Meelu and M. H. Lorretto, there is disclosed the evaluation of a Si-Ti coating, which had been applied by pack cementation at high temperatures over prolonged time periods.

The benefits of aluminising an MCrAI coating on superalloys for improved oxidation and corrosion resistance have been previously well documented. European Patent EP 897996, for example, describes the improvement of high temperature oxidation resistance of an MCrAlY on a superalloy by the application of an aluminide top coat using chemical vapour deposition techniques. Similarly, U.S. Patent 3,874,901 describes a coating system for superalloys including the deposition of an aluminum overlay onto
an MCrAlY using electron beam-physical vapour deposition to improve the hot corrosion and oxidation resistance of the coating by both enriching the near-surface of the MCrAlY with aluminum and by sealing structural defects in the overlay. Both of these systems relate to improvement of oxidation and/or hot corrosion resistance imparted to superalloys by the deposition of an MCrAlY thereon. These references do not relate to improvement of anticoking properties or corrosion resistance of high temperature stainless steel alloys used in the petrochemical industries.

A major difficulty in seeking an effective coating is the propensity of many applied coatings to fail to adhere to the tube alloy substrate under the specified high temperature operating conditions in hydrocarbon pyrolysis furnaces. Additionally, the coatings lack the necessary resistance to any or all of thermal stability, thermal shock, hot erosion, carburization, oxidation and sulfidation. A commercially viable product for olefins manufacture by hydrocarbon steam pyrolysis and for direct reduction of iron ores must be capable of providing the necessary coking and carburization resistance over an extended operating life while exhibiting thermal stability, hot erosion resistance and thermal shock resistance.

Downhole oil and gas drilling, production and casing tube strings and tools conventionally are fabricated from carbon steels which are prone to corrosion and to erosion under hostile subterranean environments. There accordingly is a need for protective surface coatings on such carbon steel components.

Plasma transferred arc surfacing (PTAS), as disclosed for example in U.S. Patents 4,878,953 and 5,624,717, is a technique used to apply coatings of different compositions and thickness onto conducting substrates. The material is fed in powder or wire form to a torch that generates an arc between a cathode and the work-piece. The arc generates plasma that heats up both the powder or wire and the surface of the substrate, melting them and creating a liquid puddle, which on solidification creates a welded coating. By varying the feed rate of material, the speed of the torch, its distance to the substrate and the current that flows through the arc, it is possible to control thickness, microstructure, density and other properties of the coating (P. Harris and B.L. Smith, Metal Construction 15 (1983) 661-666). The technique has been used in several fields to prevent high temperature corrosion, including surfacing MCrAlYs on top of nickel based superalloys

A process entitled Controlled Composition Reaction sintering Process for Production of MCrAlY coatings disclosed in Technical Report AFML-TR-76-91 by Air Force Materials Laboratory and evaluated in a report entitled Development and Evaluation of Process for Deposition of Ni/Co-Cr-AlY (McrAlY) Coatings for Gas Turbine Components disclosed in Technical Report AFML-TR-79-4097 by Air Force Materials Laboratory performed by the Solar Division of International Harvester Company Research Laboratory, San Diego, California, has been used to produce a MCrAlY type coating on super-alloys. Gas turbine blades were coated with atomized MCry-alloy using slurry containing an organic binder. The coated turbine blades were than embedded in a pack consisting of aluminum oxide (Al₂O₃), aluminum powder (Al), and ammonium chloride (NH₄Cl). The pack was heated in a controlled atmosphere under controlled time and temperature conditions to produce MCrAlY-coatings that resembled coatings deposited by a standard PVD process. The major problem with this process when applied to gas turbines is that the thickness of the coating varies and is difficult to control. In addition, the Al is added to the coating via pack aluminizing CVD process, which is environmentally unfriendly.

**Summary of the Invention**

It is therefore a principal object of the present invention to impart beneficial properties to carbon steel and stainless steel through surface alloying to substantially improve the surface properties such as by eliminating or reducing the catalytic formation of coke on the internal surfaces of tubing, piping, fittings and other ancillary furnace hardware by minimizing the number of sites for catalytic coke formation and by improving the quality of alumina scale on surface alloy coatings deposited on such steels. The alloy coatings of the invention are particularly suited for use on high temperature stainless steel for the manufacture of olefins by hydrocarbon steam pyrolysis, typified by ethylene
production, the manufacture of other hydrocarbon-based products in the petrochemical industries, and in the direct reduction of ores such as typified by the direct reduction of iron oxide ores to metallic iron in carbon-containing atmospheres.

When high temperature stainless steel tubes used in ethylene furnaces were coated with this material, an improvement on the anti-coking, anti-carburization and resistance to hot erosion properties of the tubes were observed.

It is another object of the invention to increase the carburization resistance of HTAs used for tubing, piping, fittings and ancillary furnace hardware whilst in service.

It is a further object of the invention to augment the longevity of the improved performance benefits derived from the surface alloying under commercial conditions by providing thermal stability, hot erosion resistance and thermal shock resistance.

In accordance with the present invention there are provided four embodiments of surface alloy structures generatable from the formation of a MCrAlX alloy coating directly on a high temperature stainless steel alloy substrate or onto an intermediary interlayer, followed by heat treatment to establish the coating microstructure and to metallurgically bond the coatings to the substrate. When tubes used in ethylene furnaces were treated in this way, an improvement on the anti-coking, anti-carburization and resistance to hot erosion properties of the tubes were observed.

The first embodiment of surface alloy structure of the invention comprises the application of a MCrAlX (where M = nickel, cobalt, iron or a mixture thereof and X = yttrium, hafnium, zirconium, lanthanum, scandium or combination thereof) coating material onto a high temperature stainless steel alloy substrate and an appropriate heat treatment of the MCrAlX coating and the substrate.

The second embodiment of surface alloy structure of the invention comprises depositing a layer of aluminum, or aluminum alloyed with silicon, or with silicon and at least one of chromium and titanium, on the said MCrAlX coating and heat treating the composite of aluminum or aluminum alloy, MCrAlX coating and substrate to establish the coating microstructure.

The third embodiment of surface alloy structure of the invention comprises depositing an interlayer onto the high temperature stainless steel alloy substrate beneath the MCrAlX coating. The nitrogen and carbon contents of standard high temperature
stainless steel alloys can lead to the formation of undesirable brittle nitride and carbide layers at the coating/substrate interface. The deposition of an interlayer, containing a stable nitride former, beneath the MCrAlX coating will act to disperse nitride precipitates. This is more desirable than a continuous nitride layer. The interlayer will also act to disperse carbide precipitates. Again this is more desirable than a continuous carbide layer at the coating/substrate interface. The interlayer will also increase the adherence of the MCrAlX coating to the substrate and decreases the level of surface preparation necessary for coating deposition. The MCrAlX alloy is deposited onto the interlayer, an aluminum layer is deposited onto the MCrAlX coating, and the coating system is heat-treated to diffuse aluminum into the MCrAlX coating and to metallurgically bond the layers together and to the substrate and to achieve a desired metallurgical microstructure.

The fourth embodiment of surface alloy structure of the invention comprises depositing of blended powder composition to produce a desired MCrAlXT-alloy via a reactive sintering process directly onto the substrate surface.

Each of the above embodiments optionally is pre-oxidized to form a protective outer layer of predominantly α-alumina. The α-alumina layer is highly effective at reducing or eliminating catalytic coke formation. These surface alloys are compatible with high temperature commercial processes at temperatures of up to 1150°C such as encountered in olefin manufacturing by hydrocarbon steam pyrolysis typified by ethylene production.

In its broad aspect, the method of the invention for providing a protective and inert coating to carbon steel and high temperature stainless steel substrates at temperatures up to 1150°C comprises the formation onto a steel substrate of a continuous coating of a MCrAlX alloy, where M = nickel, cobalt or iron or mixture thereof and X = yttrium, hafnium, zirconium, lanthanum, scandium or combination thereof, having 0 to 40 wt% chromium, about 3 to 30 wt% aluminum and up to about 5.0 wt%, preferably up to about 3 wt%, and more preferably, about 0.25 to 1.5 wt% of yttrium, hafnium, zirconium, lanthanum, scandium or combination thereof, the balance M. The MCrAlX alloy may be deposited by a variety of methods including but not limited to thermal spray, plasma transferred arc, physical vapour deposition and slurry coating techniques. Preferably, the overlay and substrate are heat-treated at a soak temperature in the range of about 1000 to
1200°C for at least 10 minutes, more preferably about 20 minutes to 24 hours.

The coating is deposited in a thickness of about 50 to 500 μm, preferably in a thickness about 120 to 250 μm, and most preferably about 150 μm, such as by magnetron sputtering physical vapour deposition onto the substrate at a temperature in the range of about 200 to 1000°C, preferably at about 450°C, and the coating and substrate heated to a desired soak temperature. Preferably, the MCrAlX is NiCrAlY and has, by weight, about 12 to 22% chromium, about 8 to 15% aluminum and about 0.8 to 1% yttrium, the balance nickel.

The high temperature stainless steel substrate comprises, by weight, 18 to 38% chromium, 18 to 48% nickel, the balance iron and alloying additives, and preferably is a high chromium stainless steel having 31 to 38 wt% chromium or a low chromium steel having 20 to 25 wt% chromium.

In accordance with another embodiment of the invention, a high temperature stainless steel substrate having a continuous coating of said MCrAlX alloy having a thickness of about 120 to 250 μm is aluminized by depositing a layer of aluminum thereon, and the coating with aluminum thereon and the substrate are heat-treated at a soak temperature in the range of about 1000 to 1200°C for about 20 minutes to 24 hours in an oxygen-free atmosphere to metallurgically bond the coating to the substrate and to establish a multiphased microstructure. The aluminum layer preferably is deposited on the coating in a thickness up to about 50% of the thickness of the coating, preferably up to about 20% of thickness of the coating, such as by magnetron sputtering physical vapour deposition at a temperature in the range of about 200°C to 500°C, preferably at about 300°C, and the coating with aluminum layer and substrate heated to the soak temperature.

In accordance with a further embodiment of the method of the invention, a continuous interlayer is first deposited on the substrate before the coating to disperse the formation of nitride or carbide layers at the coating/substrate interface. An effective interlayer is comprised of about 35 to 45 wt% aluminum, a total of about 5 to 20 wt% of at least one of titanium or chromium, and 40 to 55 wt% silicon, preferably about 35 to 40 wt% aluminum, about 5 to 15 wt% titanium and about 50 to 55 wt% silicon, is deposited onto a high temperature stainless steel substrate as described in co-pending application Serial No. 08/839,831 incorporated herein by reference, a continuous MCrAlX alloy
coating is deposited onto the diffusion coating, and an aluminum layer is deposited onto
the MCrAlX alloy coating.

The interlayer preferably is deposited by physical vapour deposition at a
temperature in the range of 400 to 600°C or 800 to 900°C, preferably at either 450 or
850°C. Thermal spray deposition techniques also may be used. The interlayer is then
heated to a soak temperature at a rate of temperature rise of at least 5 Celsius
degrees/minute, preferably at a rate of 10 to 20 Celsius degrees/minute, to establish the
coating microstructure. The MCrAlX coating, and preferably an aluminum layer, are
deposited such as by physical vapour deposition onto the interlayer and then heat-treated
to establish the multiphased microstructure and to metallurgically bond the coating system.

The systems subsequently can be heated in an oxygen-containing atmosphere at
a temperature above about 1000°C, preferably in the range of above 1000°C to 1160°C, in
a consecutive step or in a separate later step for a time effective to form a surface layer of
\( \gamma \)-alumina thereon.

The interlayer is deposited in a thickness of about 20 to 100 \( \mu \)m and preferably in
a thickness of about 20 to 60 \( \mu \)m. The interlayer is heat-treated at a soak temperature in
the range of about 1030 to 1150°C for a time effective to form a diffusion barrier between
the base alloy and enrichment pool containing intermetallics of silicon and one or more
of titanium or aluminum and the base alloying elements. Preferably, the interlayer
contains about 6 to 10 wt% silicon, 0 to 5 wt% aluminum, 0 to 4 wt% titanium and about
25 to 50 wt% chromium, the balance iron and nickel and any base alloying elements.

An alternative process for creating a similar coating system is the deposition of the
interlayer, MCrAlX alloy coating, and optionally the aluminum layer in sequence, and
heat-treating in an inert atmosphere at a soak temperature in the range of about 1030 to
1160°C to establish the microstructure and to bond the coatings.

It is therefore a further object of the present invention to optionally provide a
surface alloy MCrAlX coating on HTAs by a single process step without a separate heat
treatment.

In its broad aspect, this embodiment of a method of the invention for providing a
protective and inert coating to high temperature stainless steels comprises providing a
protective and inert coating on high temperature stainless steel comprising metallurgically
bonding a continuous coating of a MCrAlX alloy, where M = nickel, cobalt or iron or mixture thereof and X = yttrium, hafnium, zirconium, lanthanum, scandium or combination thereof, having about 0 to 40 wt% chromium, preferably about 10 to 25 wt% chromium, about 3 to 30 wt% aluminum, preferably about 4 to 20 wt% aluminum, and up to about 5 wt% X, preferably up to about 3 wt% X, more preferably 0.25 to 1.5 wt% X, the balance M, by plasma transferred arc deposition of the coating onto a high temperature stainless steel substrate. The coating is deposited in a thickness of about 20 μm to 6000 μm, preferably 50 to 2000 μm, more preferably 80 to 500 μm onto the substrate.

The MCrAlX may be FeCrAlY having 0 to 25 wt% chromium, about 3 to 40 wt% aluminum, up to about 3 wt% yttrium, and the balance substantially iron.

The MCrAlX preferably is NiCrAlY and has, by weight, about 12 to 25% chromium, about 4 to 15% aluminum and about 0.5 to 1.5% yttrium, the balance nickel.

In accordance with this preferred embodiment of the invention, the deposition of a dense, anti-coking NiCrAlY alloy coating in a single step on a HTA tube by plasma transferred arc deposition produces a gradual metallurgical bond between the alloy coating and substrate. The desired final thickness of the coating is between about 0.02 and 6 mm thick. The preferred thickness is in the range of 80 to 500 μm in order to keep powder costs reasonable and to not unduly decrease the inner diameter of the tube.

The NiCrAlY alloy coating provides a source of aluminum to provide an α-alumina based layer at the surface thereof by introducing an oxygen-containing gas such as air at a temperature above about 1000°C upon heating of the substrate and coating in a gaseous oxidizing atmosphere such as air at a temperature above 1000°C in a separate step, or during commercial use by the introduction of or presence of an oxygen-containing gas at operating temperatures above about 1000°C. The more complete the alumina scale the better the anticoking and anti-corrosion performance. Enhanced properties can be therefore sometimes be achieved by a further aluminizing step.

In accordance with another embodiment of the invention, however, the high temperature stainless steel substrate having a continuous coating of said MCrAlX alloy with a thickness of about 50 to 2000 μm, preferably about 80 to 500 μm, may be aluminized by depositing a layer of aluminum, or aluminum alloyed with up to about 60 wt%, preferably up to about 15 wt%, silicon, or at least about 20 wt% aluminum alloyed
with up to about 60 wt% silicon and up to a total of about 30 wt% of at least one of chromium and titanium, on the plasma transfer arc coating in a thickness up to about 50% of the coating thickness, preferably about 20% of the coating thickness, such as by thermal spray or magnetron sputtering physical vapour deposition. The system can be heated in an oxygen-containing atmosphere in a consecutive step or in a separate later step for a time effective to form a surface layer of -- alumina thereon.

It is still a further object of the present invention to provide an MCrAlX alloy additionally having silicon and/or a T element selected from the group consisting of tantalum, titanium, platinum, palladium, rhenium, molybdenum, tungsten, niobium, or combination thereof, to enhance the coating properties.

In this aspect of the invention, a MCrAlXSiT alloy is provided in which M = nickel, cobalt, iron or mixture thereof, X = yttrium, hafnium, zirconium, lanthanum, scandium, or mixture thereof, and T = tantalum, titanium, platinum, palladium, rhenium, molybdenum, tungsten, niobium, or combination thereof, having about 0 to 40 wt% chromium, about 3 to 30 wt% aluminum, up to about 5 wt% X, 0 to 40 wt% silicon, and up to about 10 wt% T, the balance M. Preferably the MCrAlXSiT alloy has about 10 to 25 wt% chromium, 4 to 20 wt% aluminum, up to 3 wt% X, up to 35 wt% silicon and up to 10 wt% T. More preferably, the X is present in amount of 0.25 to 1.5 wt%, silicon is present in amount up to 15 wt% and the T is present in amount of 0.5 to 8.0 wt%, most preferably T in the amount of 0.5 to 5.0 wt%.

In a preferred embodiment, a MCrAlXSi alloy coating comprising 22 wt% Cr, 10 wt% Al, 1 wt% Y and 3 wt% Si, the balance Ni, promoted a Cr-carbide layer at the coating/substrate interface which functioned as a diffusion barrier effective to retain aluminum within the coating. The presence of the silicon in the MCrAlX coating also improved a Cr-based scale produced by the overlay coating.

And a still further object of the invention is the application of a blended powder slurry composition to a substrate to produce a desired MCrAlX or MCrAlXSiT.

In accordance with a preferred embodiment of this aspect of the invention, a mixture of two or more powders of the constituents of a MCrAlX or MCrAlXSiT are blended with an effective amount of a binder to adherently coat a workpiece, and the workpiece with MCrAlX or MCrAlXSiT coating is heated to a temperature for reaction
sintering of the coating and adherent bonding of the coating onto the workpiece.

This method of the invention for providing a protective and inert coating to carbon steel and stainless steel at temperatures up to 1150°C can comprise depositing onto a steel substrate and metallurgically bonding thereto a continuous overlay coating of a MCrAlXSi alloy, where M = nickel, cobalt or iron or mixture thereof and X = yttrium, hafnium, zirconium, lanthanum or combination thereof, having about 0 to 25 wt% chromium, about 3 to 40 wt% aluminum, about 0 to 35 wt% silicon, and up to about 5.0 wt%, preferably about 0.25 to 1.5 wt% of yttrium, hafnium, zirconium, lanthanum, scandium or combination thereof, the balance being a minimum of 40 wt% M. The overlay coating may be deposited by a variety of methods including but not limited to physical vapour deposition (PVD), thermal spray, plasma transferred arc, and slurry coating techniques with reaction sintering occurring simultaneously with deposition or following deposition. In the case where reaction sintering does not occur during deposition, the overlay coating and substrate are heat-treated subsequently at a soak temperature in the range of about 500 to 1200°C for at least about 10 minutes to initiate reaction sintering.

The inclusion of silicon in the blended powder produces lower melting point constituents during the reaction sintering process, thereby allowing the molten alloy to wet the surface of the substrate and to produce an effective diffusion bond between the coating and the substrate. The silicon additions also are believed to prevent the formation of brittle carbides at the coating/substrate interface. At silicon concentration of 6 wt% or higher, the silicon dissolves chromium carbides formed in the substrate and re-precipitate these randomly as the silicon concentration falls below 6 wt% due to silicon diffusion into the substrate.

It is preferred to pre-react certain of the constituents with each other, such as by atomizing chromium, aluminum and silicon to form a CrAlSi powder prior to blending with nickel, NiCr, or NiAl powders, or combination thereof. Pre-reacting of powders retards the rate of exothermic reaction of the powders and reduces the amount of heat evolved during reaction sintering. The coated workpiece is heated to a temperature of at least about 500°C to 1100°C to initiate reaction sintering of the coating on the workpiece substrate and the temperature is increased up to 1200°C to provide a continuous impermeable coating bonded to the substrate without a sharp dividing line between the
coating and the substrate and to provide random distribution of aluminum nitrides at the coating/substrate interface.

In accordance with another embodiment of the present invention, the coating is deposited in a thickness of about 50 to 6000 \( \mu \text{m} \), preferably in a thickness about 120 to 500 \( \mu \text{m} \), more preferably 150 to 350 \( \mu \text{m} \), where the MCrAlXSi is NiCrAlYSi blended powder and has up to 20 wt% chromium, about 4 to 20 wt% aluminum, about 5 to 20 wt% silicon, and about 0.5 to 1.5 wt% yttrium, the balance being a minimum of 40 wt% nickel.

The high temperature stainless steel substrate comprises, by weight, 18 to 38% chromium, 18 to 48% nickel, the balance iron and alloying additives, and preferably is a high chromium stainless steel having 31 to 38 wt% chromium or a low chromium steel having 20 to 25 wt% chromium. For ethylene furnace applications the workpiece substrate preferably is high temperature stainless steel.

In accordance with another embodiment of the invention, a high temperature stainless steel substrate, continuously surface alloyed with MCrAlXSi alloy by reaction sintering within a thickness of about 150 to 500 \( \mu \text{m} \) is aluminized by depositing a surface layer of aluminum, aluminum alloy containing up to 60 wt%, preferably up to 15 wt%, silicon, or aluminum alloy containing up to 60 wt% silicon, a total of up to 30 wt% of at least one of chromium and titanium, the balance at least about 20 wt% aluminum, thereon and heat-treating at a soak temperature in the range of about 1000 to 1160°C for at least about 10 minutes preferably in an oxygen-free atmosphere to establish a multiphased microstructure. The aluminum or aluminum alloy surface layer preferably is deposited on the overlay in a thickness up to about 50%, preferably up to about 20%, of the MCrAlXSi thickness such as by magnetron sputtering physical vapour deposition at a temperature in the range of about 200° to 500°C, preferably at about 300°C, and the surface alloyed substrate with aluminum overlay is heated to the soak temperature.

The systems subsequently can be heated in an oxygen-containing atmosphere at a temperature above about 1000°C, preferably in the range of above 1000°C to 1160°C, in a consecutive step or in a separate later step for a time effective to form a surface layer of \( \alpha \)-alumina thereon.
**Brief Description of the Drawings**

The process of the invention and the products produced thereby will be described with reference to the accompanying drawings in which:

- **Figure 1** is a photomicrograph of a cross-section NiCrAlY coating deposited on a stainless steel substrate;
- **Figure 2** is a photomicrograph of the NiCrAlY coating shown in Figure 1 after heat-treatment;
- **Figure 3** is a photomicrograph of a cross-section of a NiCrAlY coating with an aluminum layer deposited thereon;
- **Figure 4** is a photomicrograph of the NiCrAlY coating with aluminum layer after heat-treatment;
- **Figure 5** is a photomicrograph of a diffusion coating deposited on a stainless steel substrate with a NiCrAlY coating deposited on the diffusion coating and an aluminum layer deposited on the overlay coating;
- **Figure 6** is a photomicrograph of the composite coating shown in Figure 5 after heat-treatment;
- **Figure 7** is a photomicrograph of an interface between NiCrAlY coating deposited by plasma transferred arc on a HTA alloy 900B;
- **Figure 8** is a photomicrograph of a NiCrAlY top surface after 500 hours of aging in air at 1150°C;
- **Figure 9** is a photomicrograph of a bulk microstructure after 500 hours of aging in air at 1150°C;
- **Figure 10** is a photomicrograph of an interface between NiCrAlY coating and a low chromium stainless steel after 500 hours aging in air at 1150°C;
- **Figure 11** is a photomicrograph of an interface between NiCrAlY coating and a high chromium stainless steel after 500 hours aging in air at 1150°C; and
- **Figure 12** is a photomicrograph of an interface between diffusion coating on a stainless steel substrate with a NiCrAlY coating thereon after heat-treatment.
Description of the Preferred Embodiment

A first embodiment of the present invention will be described with reference to Figures 1 and 2 of the drawings. A continuous coating of MCrAIx is shown deposited onto and metallurgically and adherently bonded to a substrate of a high temperature austenitic stainless steel. The MCrAIx alloy of the invention in which M is a metal selected from the group consisting of iron, nickel and cobalt or mixture thereof and X is an element selected from the group consisting of yttrium, hafnium, zirconium, lanthanum and scandium or combination thereof comprises, by weight, about 10 to 25% chromium, about 8 to 15% aluminum and up to about 3%, preferably about 0.25 to 1.5%, yttrium, hafnium, zirconium, lanthanum, scandium, or combination thereof, the balance iron, nickel or cobalt. The inclusion of these elements decreases oxide growth rate, increasing the mechanical strength of the oxide scale and functioning as sulphur-getters. The high temperature stainless steel substrate has a composition of iron, nickel or chromium in the range, by weight, of 18 to 42% chromium, 18 to 48% nickel, the balance iron and other alloying additives, and typically is a high chromium stainless steel having about 31 to 38% chromium or a low chromium stainless steel having about 20 to 25% chromium.

The substrates to which the MCrAIx coating is applied typically are high chromium or low chromium stainless steel centrifugally cast or wrought tubes or fittings such as used in an ethylene furnace and the coating is applied to the inside surfaces of such products. It has been found that application of the coating by magnetron sputtering physical vapour deposition permits application of a continuous, uniformly thick and dense coating throughout the length of the inside surfaces of the tubes and the fittings.

The coating is deposited onto the substrate at a temperature in the range of about 200 to 1000°C, preferably at about 450°C, as a continuous layer in a substantially uniform thickness of about 50 to 350 μm, preferably about 150 μm, by the magnetron sputtering. The coating is heated to a soak temperature in the range of 1000 to 1200°C for about 20 minutes to 24 hours in an oxygen-free atmosphere to metallurgically adherently bond the coating to the substrate and to develop a multiphased microstructure.

The coating provides a source of aluminum to provide an α-alumina based layer at the surface thereof by introducing an oxygen-containing gas such as air at a temperature above about 1000°C at the termination of the heat soak as a consecutive step, upon heating.
of the substrate and coating in a gaseous oxidizing atmosphere such as air at a temperature above 1000°C in a separate step, or during commercial use by the introduction of or presence of an oxygen-containing gas at operating temperatures above about 1000°C.

A second embodiment of the invention will now be described with reference to Figures 3 and 4. The coating of MCrAlX is deposited such as by magnetron sputtering on the high temperature stainless steel in a substantially uniform thickness of about 50 to 350 μm as described above, preferably about 150 μm. A uniform layer of aluminum, aluminum alloy containing up to about 60 wt%, preferably up to about 15 wt%, silicon, or aluminum alloy containing up to 60 wt% silicon, a total of up to 30 wt% of at least one of chromium and titanium, the balance at least about 20 wt% aluminum, is deposited onto the MCrAlX coating such as by magnetron sputtering at a temperature in the range of about 200 to 500°C, preferably at about 300°C, in an amount of up to about 50% of the thickness of the coating, preferably up to about 20% of the thickness of the coating. The substrate, coating and aluminum layer are heated to a soak temperature in the range of about 1000 to 1200°C for at least about 10 minutes, preferably for about 20 minutes to 24 hours in an oxygen-free atmosphere such as a vacuum to metallurgically bond the coating to the substrate and to establish the multiphased microstructure and to diffuse the aluminum layer into the coating and then preferably sequentially heated in an oxidizing atmosphere of an oxygen-containing gas for at least 20 minutes, preferably 20 minutes to 4 hours to oxidize the aluminum-rich layer and form a uniformly thick and adherent α-alumina based layer thereon. Oxidation of the aluminum layer can be effected in a subsequent and separate stage upon heating of the composite coating in an oxidizing atmosphere to a temperature typically above about 1000°C, for production of the α-alumina layer preferably in the range of about 1000 - 1150°C, or oxidation can occur during commercial operation in an oxidizing atmosphere at a temperature above about 1000°C.

The presence of the aluminum layer on the coating supplements the source of aluminum in the MCrAlX coating to maintain an effective continuous alumina layer during commercial operation. The diffusion of aluminum into the coating heals minor structural defects in the coating, whilst the enrichment of the surface of the coating near the surface with aluminum modifies the oxide growth mechanism, decreasing the number
of catalytic sites (such as Ni-oxide) in the protective alumina scale.

A third embodiment of the invention will now described with reference to Figures 5 and 6. In accordance with this embodiment of the method of the invention, a continuous aluminum-containing interlayer comprised of about 35 to 45 wt% aluminum, a total of about 5 to 20 wt% of at least one of titanium or chromium, and 40 to 55 wt% silicon, preferably about 35 to 40 wt% aluminum, about a total of about 5 to 15 wt% of at least one of titanium or chromium, and about 50 to 55 wt% silicon, are deposited onto a high temperature stainless steel base alloy substrate as described in co-pending application Serial No. 08/839,831, a continuous MCrAlX alloy coating is deposited onto the interlayer, and an aluminum or aluminum alloy which include nickel aluminides is deposited onto the overlay alloy coating.

In this embodiment, the aluminum within the interlayer combines with the nitrogen in the substrate to form a dispersion of aluminum nitride precipitate, thereby permitting scavenging of nitrogen emanating from the substrate.

The interlayer preferably is deposited by physical vapour deposition at a temperature in the range of 400 to 600°C or 800 to 900°C, preferably at either 450 or 850°C. The interlayer is then heated to a soak temperature at a rate of temperature rise of at least 5 Celsius degrees/minute, preferably at a rate of 10 to 20 Celsius degrees/minute, to establish the coating microstructure. The MCrAlX coating, and preferably an aluminum layer, are deposited by physical vapour deposition onto the interlayer and then heat-treated to establish the multiphased microstructure and to metallurgically bond the coatings.

The interlayer is deposited in a thickness of about 20 to 100 μm and preferably in a thickness of about 20 to 60 μm. The interlayer, MCrAlX coating with aluminum layer and substrate base alloy are heat treated at a soak temperature in the range of about 1030 to 1180°C for a time effective to form an interlayer between the base alloy and coating containing intermetallics of silicon and one or more of titanium or aluminum and the base alloying elements. Preferably, the interlayer after heat treatment contains about 6 to 10 wt% silicon, 0 to 5 wt% aluminum, 0 to 4 wt% titanium and about 25 to 50 wt% chromium, the balance iron and nickel and any base alloying elements.

The interlayer requires precise heat treatment to form an adequately stratified and adherent final coating. Coatings comprising for example 10 wt.% titanium, 40 wt.%
aluminum and 50 wt.% silicon are deposited in the temperature range 400° to 500°C and preferably at about 450°C using sputtering as the deposition process. It is possible to deposit the coating at temperature of up to 1000°C, but unless subsequent thermal processing is done in the same furnace, there is little incentive to coat at these higher temperatures. During the treatment, the rate of temperature rise must be at least 5°C per minute, typically in the range of 10°C to 20°C per minute, from about 500°C to within 5°C of the maximum temperature.

At temperatures between about 1130°C and 1150°C, a final segregation of the coating into layers occurs. The final microstructure obtained is strongly dependent on the temperature, but not significantly dependent on the time spent at these temperatures, within the time range of at least about 10 minutes, preferably about 20 minutes to two hours. However, a different and less desirable microstructure results if the time at the final temperature is too short, for example, for less than 10 minutes. At the lower end of this temperature range at 1130°C, void formation is still probable. The optimum temperature range for the final temperature soak is 1135°C to 1145°C for at least about 20 minutes, preferably about 30 minutes to 2 hours. At higher temperatures, the diffusion barrier that is formed becomes unstable, and at 1150°C, is quickly destroyed by inward diffusion of silicon. Above this temperature, aluminum diffusion downward also occurs, leaving an aluminum content below 5 percent. However, up to 1160°C, the aluminum content is still sufficient for the dispersion of nitrides.

If the stainless steel substrate is a wrought or cast low chromium base alloy substrate containing 20 to 25 wt.% chromium, the temperature ramp rate should be the same as for the high chromium base alloy substrate at about 10°C to 20°C per minute, but the preferred soak temperature is within the range 1030 to 1160°C. In this embodiment, the chromium silicide-containing diffusion barrier does not form due to the low chromium concentration in the base alloy. Alloys with 20 to 25 wt.% chromium content include the Inco 800™ series alloys, for example 88HT™, 800HT™ and 803™ alloys. The required minimum temperature ramp rate is not dependent on the base alloy composition.

A further embodiment of the invention will now be described with respect to Figure 12. In accordance with this embodiment of the method of the invention, an interlayer of NiCr alloy or TiAlSi alloy was deposited by magnetron sputtering in a
thickness of about 20 to 100 \(\mu m\) onto a high temperature stainless steel substrate, a MCrAlX coating was deposited onto the interlayer in one or two continuous coatings, and the resulting coated substrate heat treated at a temperature in the range of 1000 to 1180\(^\circ\)C to metallurgically bond the coatings.

These embodiments of the method of the invention will now be described with respect to the following non-limitative examples.

 Tubes and coupons of 25Cr 35Ni (800H, 803, HPM, HK4M) and selected 35Cr 45Ni alloys were coated with MCrAlX embodiments of the invention using a magnetron sputtering physical vapour deposition technique. Coated samples were heat treated at high temperatures in a vacuum in order to improve the interface adhesion of the coating to the substrate by metallurgical bonding and to develop a fine-grained metallurgical structure, and then in an oxidizing atmosphere with an aluminum surface coating on the coating to develop an oxide outerlayer surface with anti-coking properties. The top surface layer of aluminum was deposited using the same coating technique of magnetron sputtering to enhance the aluminum content of the MCrAlX coating and to improve the coating’s ability to regenerate the protective oxide surface layer while healing minor structural defects in the coating to decrease the number of catalytic sites in the alumina scale.

 When coating certain centrifugally cast 25Cr - 35Ni/35Cr - 45Ni alloys, an aluminum-bearing diffusion coating typified by a TiAlSi alloy was deposited on the substrate to function as an interlayer between the substrate and the aluminized coating to protect the coating from the outward diffusion of nitrogen from the cast alloy. Alternatively, an interlayer of a NiCr alloy can be used to disperse nitride formation.

 The coated and heat-treated samples were characterized for uniformity, metallurgical bond, microstructure, thickness and composition by standard laboratory techniques using optical microscope and scanning electron microscope with energy dispersive spectroscopy. Tests to evaluate thermal stability, resistance to oxidation, carburization, thermal shock, thermal fatigue and creep resistance were carried out and documented.

 Small test coupons and 3-foot long tubes were tested in a simulated pyrolysis test rig. A residence time of 0.4 - 3 seconds was used at a temperature in the range of 800 - 950\(^\circ\)C. Run lengths varied from 1 to 8 hours. The performance of the coated tubes and
coupon samples was compared with uncoated high-temperature alloys, ceramics and pure nickel.

Coated tubes having a length of 3 feet with OD of 5/8 inch were tested in a simulated pyrolysis test rig. The performance of the coated tubes were compared with an uncoated high temperature alloy and a quartz tube.

The coatings were uniformly deposited on the inner wall surface of the tubes and heat treated in accordance with the methods of the invention. Comparisons of the coated products with uncoated tubes and fittings were made on the basis of coking rates, carburization, ability to metallurgically adhere to the surfaces of commercially produced high chromium/nickel centrifugally cast tubes and wrought tubes under thermal shock and thermal cycling conditions, and resistance to hot erosion.

**Example 1**

With reference to Figures 1 and 2, a NiCrAlY coating 10 containing, by weight, 22% chromium, 10% aluminum and 1% yttrium, the balance nickel, was deposited on an Incoloy 800H\(^\text{TM}\) stainless steel substrate 12 by magnetron sputtering at 450°C to provide an average coating thickness of 150 \(\mu\text{m}\). The NiCrAlY coating and substrate were heat-treated in a vacuum at a rate of temperature rise of 15 Celsius degrees/minute to 1100°C and held for 1 hour at 1100°C to produce a nickel aluminate precipitate phase 14 in an alloy matrix illustrated in Figure 2.

The resulting coating was subjected to carburization for 70 16-hour cycles in a CO/H\(_2\) atmosphere at 1080°C. The coating displayed good carburization resistance. The coating was shown to maintain thermal stability for 1000 hours at 1150°C. The coating displayed superior mechanical properties (as compared to the diffusion coating), whilst stress-rupture testing indicated no significant adverse effects on substrate properties.

**Example 2**

An aluminized NiCrAlY coating 16 containing, by weight, 22% chromium, 10% aluminum and 1% yttrium, the balance nickel, was deposited on a Sandvik 800H\(^\text{TM}\) stainless steel substrate 18 by magnetron sputtering at 450°C, to provide a coating thickness of 150 to 200 \(\mu\text{m}\). An aluminum layer 22 was magnetron sputtered onto the
coating at 450°C, to give an average aluminum coating thickness of about 40 μm, shown in Figure 3.

The aluminized NiCrAlY coating and substrate were heat-treated in a vacuum at a rate of temperature rise of 15 Celsius degrees/minute and held for 1 hour at 1100°C to produce nickel aluminide phase 22 and an underlying nickel aluminide precipitate phase in an alloy matrix 26 adjacent stainless steel substrate 18. The aluminized coating was oxidized in air for 1 hour at a temperature at about 1050°C to produce an α-alumina surface layer 28.

The resulting coating was shown to have good carburization resistance, withstanding 45 (+) 16 hour cycles in a CO/H₂ atmosphere. The coating maintained thermal stability for 500 hours at 1150°C. The coating was subjected to 1000 thermal cycles at 1100°C and exhibited excellent coking resistance, similar to that of an inert ceramic.

**Example 3**

With reference to Figure 5, a diffusion coating 30 containing, by weight, 10% chromium, 40% aluminum and 50% silicon was deposited by magnetron sputtering at a temperature of 850°C, to give an average thickness of 40 μm, onto Manoir XTM™ stainless steel substrate 32. A NiCrAlY coating 34 containing, by weight, 22% chromium, 10% aluminum and 1% yttrium, the balance nickel, was deposited onto the diffusion coating by magnetron sputtering at approximately 850°C, to give an average coating thickness of 150 μm. An aluminum layer 36 was applied onto the NiCrAlY coating 34 using magnetron sputtering at 450°C, to give an average aluminum coating thickness of 20 μm.

The aluminized NiCrAlY coating on the diffusion coating was heat-treated in a vacuum at a rate of temperature rise of 15 Celsius degrees/minute and held for 1 hour at 1150°C to yield a diffusion barrier 40 on the substrate 32 and an enrichment pool 42 adjacent the diffusion barrier 40, shown in Figure 6. A nickel aluminate phase 44 is formed by the inward diffusion of the aluminum layer into the upper portion of the NiCrAlY coating 46. Nickel aluminate phase 44 developed α-alumina based layer 48 on the surface thereof as a result of adding air at the end of the vacuum heat-treatment.
The resulting coating was held at 1150°C for 500 hours to evaluate thermal stability and was also subjected to thermal shock tests. The coating exhibited good thermal stability and good resistance to thermal shock.

**Example 4**

A NiCr alloy, by weight 50% Cr, 50% Ni, was deposited onto a Kubota KHR35CW alloy by magnetron sputtering at 450°C to provide an average thickness of 40 μm. A NiCrAlY coating, by weight 22% Cr, 10% Al, 1% Y balance Ni, was deposited by magnetron sputtering at 450°C to provide an average thickness of 60 μm, followed by a second NiCrAlY coating, by weight 18% Cr, 15% Al, 1% Y balance Ni, deposited by magnetron sputtering at 450°C to provide an average thickness of 80 μm. The resultant coating and substrate were heat treated in vacuum for 1 hour at 1150°C.

The heat-treated coating was isothermally oxidized in laboratory air for 192 hours, after which the coating was still in relatively good condition. The coating also displayed good mechanical properties, as compared to a NiCrAlY without the NiCr layer.

**Example 5**

A TiAlSi alloy, by weight 20% Ti, 20% Al balance Si, was deposited onto a Manior XM alloy by magnetron sputtering at 850°C to give an average thickness of 40 μm. A NiCrAlY alloy comprising, by weight, 22% Cr, 10% Al, 1% Y balance Ni, was then deposited by magnetron sputtering at 850°C to give an average thickness of 160 μm.

The subsequent coating was heat-treated in vacuum for one hour at 1150°C to provide the interlayer illustrated in Figure 12.

The resultant coating was isothermally oxidized in laboratory air and was shown to provide protection for up to 480 hours, whilst successfully dispersing damaging nitride phases.

**Example 6**

With reference now to Figures 7 - 11, a continuous coating of MCrAlX was deposited onto and metallurgically and adherently bonded to a substrate of a high temperature austenitic stainless steel by a plasma transferred arc process. The MCrAlX
alloy of the invention in which M is a metal selected from the group consisting of iron, nickel and cobalt or mixture thereof and X is an element selected from the group consisting of yttrium, hafnium, zirconium, lanthanum, scandium and combination thereof comprises, by weight, about 0 to 40%, preferably about 10 to 25%, chromium, about 3 to 30%, preferably about 4 to 20%, aluminum, and up to about 5%, preferably up to 3%, and more preferably about 0.5 to 1.5%, yttrium, hafnium, zirconium, lanthanum, and/or scandium, the balance iron, nickel or cobalt or combination thereof.

The substrates to which the MCrAlX overlay coating is applied typically are high chromium or low chromium stainless steel centrifugally cast or wrought tubes or fittings and it has been found that application of the coating by plasma transferred arc process deposition permits application of a continuous, uniformly thick and dense coating throughout the length of the inside surfaces of the tubes and the fittings.

A preferred MCrAlX is NiCrAlY which comprises, by weight, about 12 to 25% chromium, about 4 to 15% aluminum, about 0.5 to 1.5% yttrium, and the balance substantially nickel.

The deposition process for the NiCrAlY coating involves the application of a powder raw material of the MCrAlX composition, by a plasma transferred arc process with the base alloy substrate forming part of the electric circuit. In the said process a plasma arc melts both the powder and the base alloy; argon being used as a carrier and shrouding gas to prevent oxidation. The process parameters are controlled during deposition to yield a melt puddle that will yield a coating with a desired thickness. By melting part of the substrate alloy, some dilution occurs which affects the final composition of the coating. It also produces a desired transition zone between the base alloy and the coating, which accommodates, in a scattered fashion, the carbides and nitrides formed due to the diffusion of carbon and nitrogen at the high temperatures at which ethylene furnaces operate. This significantly reduces the risk of spallation of the coatings.

The coating thus produced is dense, forms an alumina scale when exposed to air at high temperatures, and is tightly adhered to tube. The plasma transferred arc process can eliminate a separate aluminizing step. Also, the material transfer method is highly efficient and between 80 to 90% of the raw material is incorporated into the coating,
compared to between 25 and 30% with magnetron sputtering.

Two high temperature alloy stainless steel materials were used as substrates; one a H46M alloy the other one 900 B alloy. The coating was obtained from a NiCrAlY powder with a nominal composition in weight percentage of Al 10, Cr 22, Y 1, Ni balance, with impurities comprising less than 1 wt%. The size distribution of the powder was as +45 microns - 106 microns. It was fed to the gun at a rate of 30 grams per minute using 100 amps and 50 volts across the arc.

The coating was dense and continuous, over 4 mm thick, with a smooth interface as shown in Figure 7. No defects spanning from the base alloy to the coating surface were observed but some bubbles could be detected near the outer surface of the coating. The composition reflected the fact that part of the alloy was melted, so the NiCrAlY got mixed and diluted with the elements present in the HTA. In both cases the aluminum content was between 5 to 7 wt%. The sample deposited on H46M had however less iron, more nickel and chromium than the sample deposited on 900B. Some other elements present in the base alloy such as silicon, niobium and manganese diffused into the coating but none amounted to more than 1 wt% on the welded layer. No heat treatment was given to these samples prior to their examination.

The samples were aged in air at 1150°C for up to 500 hours. After each aging period the samples were taken out of the oven and dipped in water to assess the thermal shock resistance of the ensemble. None of the samples spalled or cracked after such treatments. The bulk microstructure did not drastically change after any aging time, as indicated in Figures 8 and 9. However, at the free surfaces and at the interface new structures developed. A 10 microns thick alumina layer was formed on the outer surface which proved to drastically reduce the formation of catalytic coke in coated HTA alloys. In voids and other inner defects, a core of mixed oxides (Cr-Al-Ni-Y O) was precipitated inside an alumina skin. The attack by oxygen extended several microns inside the coating. At the interface a large amount of nitrides, basically AlN, developed; these crystals grew in a dispersed manner as shown in Figures 10 and 11. The number of nitrides was larger in the sample prepared on the high chromium H46M alloy, probably due to a larger amount of nitrogen dissolved in the alloy. Even in this case, the nitrides did not agglomerate in a straight or continuous manner, hence reducing the possibility of a
mechanical failure. This avoids the need for deposition of an interlayer whose main purpose was to absorb the nitrogen coming from the tube. The amount of aluminum in the bulk was reduced to just above 5 wt% after 500 hours at aging at 1150°C, part of the original aluminum having diffused into the base alloy.

This embodiment of the method of this invention provides a number of important advantages. NiCrAlY powders are applied by plasma transferred arc to substrate alloys and the resulting interface layer is dense, continuous and smooth and forms an adherent metallurgical bond with the HTA substrate. Any precipitated nitrides and carbides are dispersed in and in proximity to the interface layer, obviating the need for heat treatment of the coating or the provision of a separate interlayer. Enough aluminum is available in the coating to form an alumina surface scale. After 500 hours of aging in air at 1150°C and thermal shock tests, the composition and bulk structure changed only slightly. Nitrides formed near the interface layer, however, these are dispersed and will not result in coating delamination. The surface region showed evidence of oxidation, however, the attack was shallow and sufficient aluminum remained to maintain the protective alumina scale. The surface alloy of the invention on HTAs has particular utility in the coating of reactor tubes for use in high temperature corrosive environments such as furnaces for the production of ethylene.

The additive silicon can be present in the amount of 0 to about 40 wt%, preferably 3 to 15 wt%. The additive T can be present in an amount of 0 to 10 wt%, preferably 0.1 to 5 wt%, and more preferably 0.5 to 3 wt%. A preferred additive T is titanium, tantalum, platinum or palladium, tungsten, molybdenum, niobium or rhenium in an MCrAlX comprised of about 12 to 25 wt% chromium, about 4 to 15 wt% aluminum, about 0.5 to 1.5 wt% yttrium, the balance nickel. The addition of silicon to the MCrAlX coating improves the resistance to both hot corrosion and oxidation. The addition of tantalum and tungsten in Cr-based coatings imparts improved resistance to sulphidation and oxidation. The presence of molybdenum to an aluminum-forming alloy improves the quality of the Cr-based oxide scale which forms once aluminum has been deleted from the coating alloy. The inclusion of titanium in the MCrAlX alloy composition improves the coatings resistance to hot corrosion, particularly resistance to sulphide and/or halide bearing compounds. Niobium additions strengthen the coating, altering the coating thermal
expansion coefficient to match the thermal expansion of the substrate. The presence of palladium, platinum or rhenium provides a superior, slower growing alumina scale. A preferred composition is MCrAlXSi comprising 22 wt% Cr, 10 wt% Al, 1 wt% Y, 3 wt% Si, the balance nickel.

5 The thickness of the MCrAlXSi or MCrAlXT overlay coating may vary from 20 to 6000 μm, preferably 50 to 2000 μm, and more preferably 80 to 500 μm in thickness.

A surface layer of aluminum, aluminum alloy containing up to 50 wt%, preferably up to 15 wt%, of silicon, or aluminum alloy containing up to 60 wt% silicon, a total of up to 30 wt% of at least one of chromium and titanium, the balance at least about 20 wt% aluminum, may be deposited onto the MCrAlXSi or MCrAlXT coating in an amount up to 50% of the thickness of the coating. A preferred top layer is a layer of aluminum or aluminum alloy having a thickness up to 20% of the thickness of the MCrAlSi or MCrAlXT overlay coating.

An industrial embodiment of the coating of the invention is a coking and corrosion resistant reactor tube for use in high temperature environments comprising an elongated tube of a high temperature stainless steel and a continuous coating metallurgically bonded on the inner surface of the elongated tube comprising a MCrAlXT alloy wherein M is nickel, cobalt, iron or a mixture thereof, X is yttrium, hafnium, zirconium, lanthanum, scandium or combination thereof, and T is silicon, tantalum, titanium, platinum, palladium, rhenium, molybdenum, tungsten, niobium or combination thereof, and comprising, by weight, about 10 to 25% chromium, about 4 to 20% aluminum, up to about 3 wt% X, and up to about 8 wt% T, the balance M, deposited by one of several methods including physical vapor deposition, plasma thermal spray or plasma transferred arc surfacing, or applied by a binder coating, and wherein the MCrAlXT coating has a thickness of about 20 μm to 6000 μm.

It has been found that a MCrAlXSi coating silicon is present in an amount of 3 to 40 wt% can be applied to a substrate of carbon steel or low-grade or high-temperature stainless steels such as tubes and fittings by adding a blended powder of two or more of the MCrAlXSi constituents to an organic binder to form a slurry and coating the substrate with the slurry. The coated substrate is dried and heated in a vacuum furnace for evaporation of the organic binder and for reaction sintering of the coating with the
substrate for adhesion of the coating to the substrate.

A preferred slurry composition comprises at least two powder constituents of MCrAlXSi of which M is nickel. The powder is blended and is added to an organic binder such as an acrylic binder dissolved in an organic solvent. The nickel has a relatively smaller average size of 2 to 10 μm, compared to the average size of 50 to 150 μm for the remaining constituent or constituents, and has an irregular shape compared to the rounded or spherical shape of the remaining constituent or constituents. The size and shape variations permit the particles to interlock and to remain on the substrate once the organic binder has evaporated, to be described.

The inclusion of up to 40 wt% silicon in the blended powder lowers the melting point of the coating to about 900 to 1150°C. At silicon concentration of 6 wt% or higher, the silicon dissolves chromium carbides formed in the substrate and re-precipitate these randomly as the silicon concentration falls below 6 wt% due to silicon diffusion into the substrate.

In accordance with this aspect of the invention, there are provided five embodiments of surface alloy structures generatable from the deposition of two or more powders of the constituents of a MCrAlXSi alloy, and the heating of the workpiece with the coating in a vacuum or an oxygen-free atmosphere to a temperature for reaction sintering of the MCrAlXSi alloy and diffusion bonding of the alloy to the substrate.

In a first embodiment of the invention two or more powders of the constituents of MCrAlYSi alloy are blended together and isostatic pressed onto the workpiece surface. The workpiece with the pressed overlay coating is heated in a vacuum or in an oxygen-free atmosphere until the reaction sintering takes place. In reaction sintering, it is necessary to balance the chemical activity of the components in order to avoid a violent reaction. When coatings are being produced the reaction should also occur at a temperature where adhesion of the coatings to the substrate will take place. An example of an uncontrolled reaction is given by the formation of NiAl intermetallic from Ni and Al powders. The reaction between Ni and Al starts at 800 to 900°C. The temperature rises rapidly to ~1600°C, producing molten droplets of NiAl on a relatively cold substrate surface. The droplets quickly solidify and do not react with the substrate because of the low substrate temperature and high chemical stability of NiAl. In accordance with the present invention,
the activity of the powder is controlled in order to avoid a violent reaction between powders. Some of the constituents, such as Si and Al, are pre-reacted to lower their activity. For example, atomized CrAlSi powder can be blended with a combination of Ni, NiAl and NiCr powders. This reduces the amount of heat evolved during the reaction and the reaction occurs at higher temperatures. At elevated temperatures the coating reacts with the substrate surface producing an excellent coating/substrate bond. The addition of Si to the coating is necessary to produce low melting point liquids (900-1000°C) with Fe and Ni. These liquids wet the surface of the substrate and produce bonding between the coating and the substrate. The Si additions are also used to prevent the formation of brittle carbides at the coating/substrate interface. At initial concentrations of 6 wt% or higher, Si dissolves the chromium carbides found in the substrate and re-precipitates them randomly as the Si concentration falls below 6% Si due to diffusion into the substrate.

In a second embodiment of the invention, two or more powders of the constituents of MCrAlYSi-alloy are blended together and deposited as a coating onto the workpiece surface by thermal spray, chemical vapour deposition or by magnetron sputtering from a previously thermal sprayed cathode. The workpiece with coating is then heated in a vacuum or in an oxygen-free atmosphere until the reaction sintering takes place.

In a third embodiment of the invention, two or more powders of the constituents of MCrAlYSi-alloy are blended together and deposited onto the workpiece surface by plasma transferred arc process, which performs the reaction sintering process simultaneously with the deposition.

In a fourth embodiment of the invention, two or more powders of the constituents of MCrAlYSi-alloy are blended with an effective amount of an organic binder if necessary, and mixed with a solvent combined with a viscous transporting agent in order to be deposited as slurry onto the workpiece surface. The workpiece, with the overlay slurry coating is dried prior to heating in vacuum or in oxygen free atmosphere until the reaction sintering takes place.

One of the advantages of the reaction sintering process is that a sharp dividing line between the coating and the substrate is not formed. Not only does it result in better bonding between the coating and the substrate but in the case of MCrAlY alloys on a nitrogen containing substrate it will result in a random distribution of brittle aluminum
nitrides. In an MCrAlY coating deposited by the PVD process these nitrides can form brittle layers at the coating/substrate interface resulting in coating delamination.

The coating provides a source of aluminum to provide an $\alpha$-alumina based layer at the surface thereof by introducing an oxygen-containing gas such as air at a temperature above about 1000°C at the termination of the heat soak as a consecutive step, upon heating of the substrate and coating in a gaseous oxidizing atmosphere such as air at a temperature above 1000°C in a separate step, or during commercial use by the introduction of or presence of an oxygen-containing gas at operating temperatures above about 1000°C.

The fifth embodiment of surface alloy structure of the invention comprises depositing a layer of aluminum on top of the said MCrAlXSi surface alloy structure and heat treating the composite of aluminum and MCrAlXSi surface alloyed substrate to establish the desired coating microstructure.

It will be understood, of course, that modifications can be made in the embodiments of the invention illustrated and described herein without departing from the scope and purview of the invention as defined by the appended claims.
We claim:

1. A method for providing a protective coating having a non-catalytic surface on low-carbon steel and stainless steel comprising depositing onto a steel substrate and metallurgically bonding thereto a continuous coating of a MCrAlX alloy, where M = nickel, cobalt or iron or mixture thereof and X = yttrium, hafnium, zirconium, lanthanum, scandium or combination thereof, having about 0 to 40 wt% chromium, about 3 to 40 wt% aluminum and up to about 5 wt% X, the balance M.

2. A method as claimed in claim 1 in which the substrate is a high temperature stainless steel and the MCrAlX alloy comprises about 10 to 25 wt% chromium, about 5 to 20 wt% aluminum and up to about 3 wt% X, the balance M.

3. A method as claimed in claim 2, metallurgically bonding the coating to the substrate by heat-treating the coating and substrate to a soak temperature for a time effective to provide a multiphased microstructure change and to metallurgically bond the coating to the substrate.

4. A method as claimed in claim 3 in which X is present in an amount of 0.25 to 1.5 wt% and in which the coating is deposited in a thickness of about 50 to 500 μm and the coating and substrate are heated to a soak temperature in the range of about 1000 to 1200°C and maintained at said soak temperature for at least about 10 minutes.

5. A method as claimed in claim 4 in which the MCrAlX is NiCrAlY and has about 12 to 22 wt% chromium, about 8 to 20 wt% aluminum and 0.8 to 1 wt% yttrium, the balance nickel, and in which the coating is deposited by magnetron sputtering physical vapour deposition onto the substrate in a thickness of about 50 to 350 μm at a temperature in the range of about 200 to 1000°C.

6. A method as claimed in claim 4 additionally comprising depositing a surface layer of aluminum, aluminum alloy containing up to 50 wt% silicon, or aluminum alloy containing up to 60 wt% silicon, a total of up to 30 wt% of at least one of chromium and titanium, the balance at least about 20 wt% aluminum, and having a thickness of up to about 50% of the coating onto the coating and heat-treating the coating with aluminum or aluminum alloy thereon and the substrate at the soak temperature in an oxygen-free atmosphere to diffuse the surface layer into the coating and to metallurgically bond the coating overlay to the substrate, optionally followed by heat-treating in an oxidizing
atmosphere to form an alumina surface scale thereon.

7. A method as claimed in claim 6 in which an aluminum alloy contains up to 15 wt% silicon and depositing the aluminum or aluminum alloy on the coating in a thickness of about 20% of the thickness of the coating by magnetron sputtering physical vapour deposition at a temperature in the range of about 200 to 500°C and heat-treating in an oxidizing atmosphere at a temperature in the range of about 1000°C to 1160°C for a time effective to form the alumina scale thereon.

8. A method as claimed in claim 6 additionally comprising depositing a continuous layer onto the stainless steel substrate before depositing the continuous MCrAlX coating to provide an interlayer between the stainless steel substrate and the coating effective to minimize or avoid the formation of continuous nitride or carbide layers at the coating and substrate interface.

9. A method as claimed in claim 8 in which the interlayer is comprised of about 35 to 45 wt% aluminum, about 5 to 20 wt% of at least one of chromium or titanium, and about 40 to 55 wt% silicon deposited onto the high temperature stainless steel substrate in a thickness of about 20 to 100 μm at a temperature in the range of 400 to 600°C or 800 to 900°C, and heat-treating said interlayer at a soak temperature in the range of about 1030 to 1180°C for at least about 20 minutes.

10. A method as claimed in claim 9 in which the stainless steel substrate contains about 31 to 38 wt% chromium and heat-treating said interlayer for about 30 minutes to 2 hours at a soak temperature in the range of about 1130 to 1160°C.

11. A method as claimed in claim 9 in which the stainless steel substrate contains about 20 to 25 wt% chromium and heat-treating said interlayer for about 30 minutes to 2 hours at a soak temperature in the range of about 1050 to 1160°C.

12. A method as claimed in claim 8 in which the interlayer is comprised of about 35 to 45 wt% aluminum, a total of about 5 to 15 wt% of at least one of chromium or titanium, and about 50 to 55 wt% silicon deposited onto a high temperature stainless steel substrate, depositing a continuous MCrAlX alloy coating, where M = nickel, cobalt or iron or mixture thereof and X = yttrium, hafnium, zirconium, lanthanum, scandium or combination thereof, having about 10 to 25 wt% chromium, about 6 to 15 wt% aluminum and up to about 3 wt% X, the balance M, onto the interlayer, optionally depositing an
aluminum layer onto the MCrAlX alloy coating, heat-treating the substrate, interlayer, coating and aluminum or aluminum alloy surface layer at a soak temperature in an oxygen-free atmosphere for a time effective to diffuse the surface layer into the coating, to provide a multiphased microstructure and to metallurgically bond the coating and interlayer to the substrate, and subsequently optionally heat-treating in an oxidizing atmosphere at a temperature above about 1000°C for a time effective to form an alumina surface scale thereon.

13. A method as claimed in claim 12 in which the coating and substrate are heated to a soak temperature in the range of about 1030 to 1180°C for about 20 minutes to 24 hours.

14. A method as claimed in claim 12 in which the interlayer is deposited by magnetron sputtering physical vapour deposition at a temperature in the range of 800 to 900°C and the interlayer, the MCrAlX coating with the aluminum or aluminum alloy surface layer, and the substrate are heated to a soak temperature at a rate of temperature rise of at least 5 Celsius degrees/minute.

15. A method as claimed in claim 14 in which the interlayer, the MCrAlX coating with the aluminum or aluminum alloy surface layer and the substrate are heated to the soak temperature at a rate of about 10 to 20 Celsius degrees/minute.

16. A method as claimed in claim 15 in which the interlayer is deposited in a thickness of about 20 to 100 μm and the interlayer, MCrAlX coating with aluminum or aluminum alloy surface layer and substrate base alloy are heat treated at a soak temperature in the range of about 1030 to 1160°C for a time effective to form an interlayer between the base alloy and enrichment pool containing intermetallics of silicon and one or more of titanium or aluminum and the base alloying elements.

17. A method as claimed in claim 16 in which the interlayer contains after heat treatment about 6 to 10 wt% silicon, 0 to 5 wt% aluminum, 0 to 4 wt% titanium and about 25 to 50 wt% chromium, the balance iron and nickel and any base alloying elements.

18. A method as claimed in claim 17 in which the stainless steel substrate contains about 31 to 38 wt% chromium and heat-treating said interlayer for about 30 minutes to 2 hours at a soak temperature in the range of about 1130 to 1160°C.

19. A method as claimed in claim 17 in which the stainless steel substrate contains about 20 to 25 wt% chromium and heat-treating said interlayer for about 30 minutes to 2
hours at a soak temperature in the range of about 1050 to 1160°C.

20. A surface alloyed component comprising a stainless steel base alloy substrate and a continuous coating deposited thereon of MCrAlX alloy in which M is nickel, cobalt, iron or a mixture thereof and X = yttrium, hafnium, zirconium, lanthanum, scandium or combination thereof and comprising, by weight, about 10 to 25% chromium, about 5 to 20% aluminum and up to about 3% yttrium, hafnium, zirconium, lanthanum, scandium or combination thereof, the balance M, heat-treated at a temperature effective to metallurgically bond the MCrAlX alloy to the substrate and to provide a multiphased microstructure to the MCrAlX alloy.

21. A surface alloyed component as claimed in claim 20 in which X is present in an amount of 0.25 to 1.5 wt% and in which the coating and substrate are heated to a soak temperature in the range of about 1000 to 1180°C for about 20 minutes to 24 hours.

22. A surface alloyed component as claimed in claim 21 in which the MCrAlX is NiCrAlY comprising, by weight, about 12 to 22% chromium, about 8 to 13% aluminum, about 0.8 to 1% yttrium, and the balance substantially nickel.

23. A surface alloyed component as claimed in claim 21 in which the coating is deposited onto the stainless steel substrate by magnetron sputtering.

24. A surface alloyed component as claimed in claim 23 in which the coating has a thickness of about 50 to 350 μm.

25. A surface alloyed component as claimed in claim 21 additionally comprising a surface layer of aluminum, aluminum alloy containing up to 50 wt% silicon, or aluminum alloy containing up to 60 wt% silicon, a total of up to 30 wt% of at least one of chromium and titanium, the balance at least about 20 wt% aluminum, having a thickness of up to about 50% of the coating thickness metallurgically bonded to the coating.

26. A surface alloyed component as claimed in claim 25 in which the aluminum or aluminum alloy surface layer is deposited onto the coating in a thickness of up to about 20% of the coating thickness by magnetron sputtering and is oxidized in an oxidizing atmosphere at a temperature above about 1000°C for a time effective to form a protective alumina scale thereon.

27. A surface alloyed component as claimed in claim 20 additionally comprising an interlayer deposited onto the substrate between the substrate and the coating and
metallurgically bonded to the substrate and the coating effective to minimize or avoid the
formation of continuous nitride or carbide layers at the coating and substrate surface.
28. A surface alloyed component as claimed in claim 27 in which the interlayer has
a thickness of about 20 to 100 \( \mu \text{m} \) and comprises, by weight, about 35 to 45% aluminum,
about 5 to 15% titanium or chromium, and about 45 to 55% silicon.
29. A surface alloyed component as claimed in claim 20 additionally comprising an
interlayer having a thickness of about 20 to 100 \( \mu \text{m} \) deposited onto the substrate between
the substrate and the MCrAlX coating, said interlayer comprising, by weight about 50%
chromium and about 50% nickel or about 20% titanium, 20% aluminum and the balance
silicon.
30. A surface alloyed component as claimed in claim 28 in which the interlayer has
a thickness of about 20 to 60 \( \mu \text{m} \) prior to heat-treatment.
31. A surface alloyed component as claimed in claim 28 in which the interlayer, after
heat-treatment, has a diffusion barrier between the stainless steel substrate and the coating
containing intermetallics of silicon and one or more of titanium or aluminum and the base
alloying elements.
32. A surface alloyed component as claimed in claim 30 in which the interlayer, after
heat-treatment, has a diffusion barrier between the stainless steel and coating containing
about 6 to 10 wt% silicon, 0 to 5 wt% aluminum, 0 to 4 wt% titanium and about 25 to 50
wt% chromium, the balance iron and nickel and any base alloying elements.
33. A coking and corrosion resistant reactor tube or fitting for use in high temperature
environments comprising an elongated tube or fitting formed from a high temperature
stainless steel alloy and a continuous coating deposited on an inner surface of the
elongated tube or fitting comprising a MCrAlX alloy wherein M is Ni, Co, Fe or a mixture
thereof and X is yttrium, hafnium, zirconium, lanthanum, scandium or combination
thereof and comprising, by weight, about 10 to 25% chromium, about 5 to 20% aluminum
and up to about 3% yttrium, hafnium, zirconium, lanthanum or scandium, the balance M,
heat-treated at a temperature effective to metallurgically bond the MCrAlX alloy coating
to the inner surface of the elongated tube or fitting and to provide a multiphased
microstructure to the MCrAlX alloy coating.
34. A coking and corrosion resistant reactor tube or fitting as claimed in claim 33
additionally comprising a surface layer of aluminum, aluminum alloy containing up to 50 wt% silicon, or aluminum alloy containing up to 60 wt% silicon, a total of up to 30 wt% of at least one of chromium and titanium, the balance at least about 20 wt% aluminum, having a thickness of up to about 50% of the coating thickness metallurgically bonded to the coating and having an alumina scale thereon.

35. A coking and corrosion resistant reactor tube or fitting as claimed in claim 33 additionally comprising an interlayer comprising, by weight, about 35 to 45% aluminum, about 5 to 15% chromium or titanium, and about 45 to 55% silicon, deposited onto the inner surface of the elongated tube or fitting as an interlayer between the stainless steel substrate and the coating and metallurgically bonded to the inner surface of the elongated tube and the coating.

36. A coking and corrosion resistant reactor tube or fitting as claimed in claim 35 in which the interlayer prior to heat-treatment has a thickness of about 20 to 100 \( \mu \text{m} \).

37. A coking and corrosion resistant reactor tube or fitting as claimed in claim 36 in which the interlayer has a diffusion barrier between the stainless steel substrate and the enrichment pool containing intermetallics of silicon and one or more of titanium or aluminum and the base alloying elements.

38. A coking and corrosion resistant reactor tube or fitting as claimed in claim 36 in which the interlayer has a diffusion barrier between the stainless steel and coating containing about 6 to 10 wt% silicon, 0 to 5 wt% aluminum, 0 to 4 wt% titanium and about 25 to 50 wt% chromium, the balance iron and nickel and any base alloying elements.

39. A coking and corrosion resistant reactor tube or fitting produced by the method of claim 4.

40. A coking and corrosion resistant reactor tube or fitting produced by the method of claim 7.

41. A coking and corrosion resistant reactor tube or fitting produced by the method of claim 16.

42. A furnace for the production of ethylene including a plurality of reactor tubes each comprising an elongated tube formed from a high temperature stainless steel alloy and a continuous coating deposited on an inner surface of the elongated tube comprising a
MCrAlX alloy wherein M is Ni, Co, Fe or a mixture thereof and X is yttrium, hafnium, zirconium, lanthanum, scandium or combination thereof and comprising, by weight, about 10 to 25% chromium, about 5 to 20% aluminum and about 0.25 to 1.5% yttrium, hafnium, zirconium, lanthanum, scandium, or combination thereof, the balance M, heat-treated at a temperature effective to metallurgically bond the MCrAlX alloy overlay to the inner surface of the elongated tube and to provide a multiphased microstructure to the MCrAlX alloy overlay.

A furnace as claimed in claim 42 in which each reactor tube additionally comprises a surface layer of aluminum, aluminum alloy containing up to 50 wt% silicon, or aluminum alloy containing up to 60 wt% silicon, a total of up to 30 wt% of at least one of chromium and titanium, the balance at least about 20 wt% aluminum, having a thickness of up to 50% of the coating thickness metallurgically bonded to the MCrAlX coating and having an alumina scale thereon.

A furnace as claimed in claim 43 in which each reactor tube additionally comprises an interlayer having a thickness of about 20 to 100 \( \mu \text{m} \) comprising, by weight, about 35 to 45% aluminum, about 5 to 15% titanium, and about 45 to 55% silicon, deposited onto the inner surface of the elongated tube between the stainless steel substrate and the coating and metallurgically bonded to the inner surface of the elongated tube and the coating.

A method for providing a protective and inert coating on high temperature stainless steel comprising metallurgically bonding a continuous coating of a MCrAlX alloy, where M = nickel, cobalt or iron or mixture thereof and X = yttrium, hafnium, zirconium, lanthanum, scandium or combination thereof, having about 0 to 40 wt% chromium, about 3 to 30 wt% aluminum and up to about 5 wt% X, the balance M, by plasma transferred arc deposition of the coating onto the high temperature stainless steel substrate.

A method as claimed in claim 45, wherein said MCrAlX alloy has about 10 to 25 wt% chromium, 4 to 20 wt% aluminum and up to 3 wt% X.

A method as claimed in claim 45 in which the coating is deposited in a thickness of about 20 \( \mu \text{m} \) to 6000 \( \mu \text{m} \) onto the substrate

A method as claimed in claim 47, in which the coating is deposited in a thickness of about 50 to 2000 \( \mu \text{m} \) and in which X is present in an amount of 0.25 to 1.5 wt%.
49. A method as claimed in claim 47, in which the coating is deposited in a thickness of about 80 to 500 \( \mu \text{m} \).

50. A method as claimed in claim 45, wherein the MCrAlX is FeCrAlY having 0 to 25 wt% chromium, about 3 to 40 wt% aluminum, up to about 3 wt% yttrium, and the balance substantially iron.

51. A method as claimed in claim 48 in which the MCrAlX is NiCrAlY and has, by weight, about 12 to 25% chromium, about 4 to 15% aluminum and about 0.5 to 1.5% yttrium, the balance nickel.

52. A method as claimed in claim 47 additionally comprising depositing a surface layer of aluminum, aluminum alloy containing up to 50 wt% silicon, or aluminum alloy containing up to 60 wt% silicon, a total of up to 30 wt% of at least one of chromium and titanium, the balance at least about 20 wt% aluminum, having a thickness up to about 50% of the coating thickness on the coating and heat-treating the coating with aluminum thereon and the substrate to diffuse aluminum into the coating.

53. A method as claimed in claim 52, wherein the layer of aluminum or aluminum alloy has a thickness of up to about 20% of the coating thickness deposited on the coating.

54. A surface alloyed component comprising a stainless steel base alloy substrate and a continuous coating deposited thereon by plasma transfer arc deposition of MCrAlX alloy in which M is nickel, cobalt, iron or a mixture thereof and \( X = \text{yttrium, hafnium, zirconium, lanthanum, scandium or combination thereof} \) and comprising, by weight, about 0 to 40% chromium, about 3 to 30% aluminum and up to about 5% yttrium, hafnium, zirconium, lanthanum or combination thereof, the balance M, wherein the MCrAlX alloy coating has a thickness of about 20 to 6000 \( \mu \text{m} \) and is metallurgically bonded to the stainless steel substrate.

55. A surface alloyed component comprising a stainless steel substrate and an MCrAlX alloy as claimed in claim 54, in which the MCrAlX alloy has about 4 to 20 wt% aluminum, 10 to 25 wt% chromium and up to 3 wt% \( X \).

56. A surface alloyed component as claimed in claim 55 in which \( X \) is present in an amount of 0.25 to 1.5 wt%.

57. A surface alloyed component as claimed in claim 56 in which the MCrAlX is NiCrAlY comprising, by weight, about 12 to 25% chromium, about 4 to 15% aluminum,
about 0.5 to 1.5 wt% yttrium, and the balance substantially nickel.

58. A surface alloyed component as claimed in claim 55 in which the coating has a thickness of about 80 to 500 μm.

59. A surface alloyed component as claimed in claim 58 additionally comprising an aluminum surface layer having a thickness of up to about 50% of the coating thickness metallurgically bonded to the coating.

60. A surface alloyed component as claimed in claim 59 in which the aluminum surface layer has a thickness of about 20% of the coating thickness and a protective alumina scale thereon.

61. A surface alloyed component as claimed in claim 54 in which the MCrAlX is FeCrAlY comprising, by weight, about 0 - 25% chromium, about 3 to 40% aluminum, up to about 3% yttrium, and the balance substantially iron.

62. A coking and corrosion resistant reactor tube for use in high temperature environments comprising an elongated tube formed from a high temperature stainless steel and a continuous coating metallurgically bonded on an inner surface of the elongated tube comprising a MCrAlX alloy wherein M is Ni, Co, Fe or a mixture thereof and X is yttrium, hafnium, zirconium, lanthanum, scandium or combination thereof and comprising, by weight, about 10 to 25% chromium, about 4 to 20% aluminum and up to about 3% yttrium, hafnium, zirconium, lanthanum, or scandium or combination thereof by plasma transferred arc deposition of the coating onto the inner surface of the elongated tube, and wherein the MCrAlX coating has a thickness of about 20 to 6000 μm and is metallurgically bonded to the stainless steel substrate.

63. A coking and corrosion resistant reactor tube for use in high temperature environments comprising an elongated tube formed from a high temperature stainless steel and a continuous coating metallurgically bonded on an inner surface of the elongated tube comprising a MCrAlX alloy wherein M is iron and Y is yttrium, and comprising, by weight, about 0 to 25% chromium, about 3 to 40% aluminum and up to about 3% yttrium by plasma transferred arc deposition of the coating onto the inner surface of the elongated tube, and wherein the MCrAlX coating has a thickness of about 20 to 6000 μm and is metallurgically bonded to the stainless steel substrate.

64. A coking and corrosion resistant reactor tube as claimed in claim 57 additionally
comprising an aluminum surface layer having a thickness of up to 20% of the coating thickness metallurgically bonded to the coating and having an alumina scale thereon.

65. A coking and corrosion resistant reactor tube produced by the method of claim 48.
66. A coking and corrosion resistant reactor tube produced by the method of claim 51.

5 67. A coking and corrosion resistant reactor tube produced by the method of claim 53.

68. A furnace for the production of ethylene including a plurality of reactor tubes each comprising an elongated tube formed from a high temperature stainless steel and a continuous coating of a MCrAlX alloy wherein M is Ni, Co, Fe or a mixture thereof and X is yttrium, hafnium, zirconium, lanthanum, scandium or combination thereof and comprising, by weight, about 10 to 40% chromium, about 3 to 30% aluminum and up to 5% yttrium, hafnium, zirconium and/or lanthanum, the balance M, deposited in a thickness of about 20 to 6000 μm and metallurgically bonded to the inner surface of the elongated tube by plasma transfer arc deposition.

69. A furnace as claimed in claim 68 in which each reactor tube additionally comprises a surface layer of aluminum, aluminum alloy containing up to 50 wt% silicon, or aluminum alloy containing up to 60 wt% silicon, a total of up to 30 wt% of at least one of chromium and titanium, the balance at least about 20 wt% aluminum, having a thickness of about 50% of the coating thickness metallurgically bonded to the coating and having an alumina scale thereon.

70. A furnace as claimed in claim 68 in which the MCrAlX is NiCrAlY having, by weight, about 10 to 25% chromium, about 4 to 20% aluminum and about 0.5 to 1.5% yttrium, the balance nickel.

71. A method as claimed in claim 1, in which the MCrAlX additionally comprises up to about 40 wt% of silicon and up to about 10 wt% of an element T selected from the group consisting of tantalum, titanium, platinum, palladium, rhenium, molybdenum, tungsten, niobium, or combination thereof, and metallurgically bonding the coating to the substrate by heat-treating the coating and substrate to a soak temperature for a time effective to provide a multiphased microstructure change and to metallurgically bond the coating to the substrate.

72. A surface alloyed component comprising a high temperature stainless steel substrate tube and a coating of MCrAlXSiT alloy, where M = nickel, cobalt, iron or
mixture thereof, X = yttrium, hafnium, zirconium, lanthanum, scandium, or mixture thereof, and T = tantalum, titanium, platinum, palladium, rhenium, molybdenum, tungsten, niobium or combination thereof, having about 0 to 40 wt% chromium, about 1 to 30 wt% aluminum, up to about 5 wt% X, up to about 40 wt% silicon, and up to about 10 wt% T, the balance M.

73. A surface alloyed component claimed in claim 72, wherein a said MCrAlXSiT alloy has about 10 to 25 wt% chromium, 5 to 20 wt% aluminum, up to 3 wt% X, up to 15 wt% silicon and up to 10 wt% T.

74. A surface alloyed component claimed in claim 73, in which X is present in the range of 0.25 to 1.5 wt%.

75. A surface alloyed component claimed in claim 73, in which silicon is present in the range of about 3 to 15 wt%.

76. A surface alloyed component claimed in claim 73, in which T is present in the range of 0.1 to 5.0 wt%.

77. A surface alloyed component claimed in claim 73, in which T is present in the range of 0.5 to 3.0 wt%.

78. A surface alloyed component claimed in claim 72, in which the thickness of the coating is from 20 μm to 6000 μm.

79. A surface alloyed component claimed in claim 72, in which the thickness of the coating is from 50 μm to 2000 μm.

80. A surface alloyed component claimed in claim 72, in which the thickness of the coating is from 80 μm to 500 μm.

81. A surface alloyed component claimed in claim 72, in which the MCrAlXSiT alloy is NiCrAlXSi and has about 12 to 25 wt% chromium, about 4 to 15% aluminum, about 0.5 to 1.5 wt% X, up to about 15 wt% silicon and the balance nickel.

82. A surface alloyed component claimed in claim 73, in which the MCrAlXSiT is NiCrAlXTi and has about 12 to 25 wt% chromium, about 4 to 15% aluminum, about 0.5 to 1.5 wt% yttrium, up to about 5 wt% titanium and the balance nickel.

83. A surface alloyed component claimed in claim 73, in which the MCrAlXSiT is NiCrAIYTa and has about 12 to 25 wt% chromium, about 4 to 15 % aluminum, about 0.5 to 1.5 wt% yttrium, about 0.5 to 5 wt% tantalum and the balance nickel.
84. A surface alloyed component claimed in claim 73, in which the MCrAlXSiT is NiCrAlYPt and has about 12 to 25 wt% chromium, about 4 to 15% aluminum, about 0.5 to 1.5 wt% yttrium, about 0.5 to 5 wt% platinum and the balance nickel.

85. A surface alloyed component claimed in claim 73, in which the MCrAlXSiT is NiCrAlYPd and has about 12 to 25 wt% chromium, about 4 to 15% aluminum, about 0.5 to 1.5 wt% yttrium, about 0.5 to 5 wt% palladium and the balance nickel.

86. A surface alloyed component claimed in claim 73, additionally comprising a surface layer in a thickness up to about 50% of the thickness of MCrAlXSiT layer.

87. A surface alloyed component claimed in claim 84, wherein the aluminum alloy contains up to about 15 wt% silicon and has a thickness of up to 20% of the MCrAlXSiT coating.

88. A coking and corrosion resistant reactor tube for use in high temperature environments comprising an elongated tube of a high temperature stainless steel and a continuous coating metallurgically bonded on the inner surface of the elongated tube comprising a MCrAlXSiT coating wherein M is nickel, cobalt, iron or a mixture thereof, X is yttrium, hafnium, zirconium, lanthanum, scandium or combination thereof, and T is tantalum, titanium, platinum, palladium, rhenium, molybdenum, tungsten, niobium or combination thereof, and comprising, by weight, about 10 to 25% chromium, about 4 to 20% aluminum, up to about 3 wt% X, up to 15 wt% silicon and up to about 5 wt% T, the balance M, deposited by physical vapor deposition, plasma thermal spray or plasma transferred arc surfacing, and wherein the MCrAlXSiT coating has a thickness of about 20 μm to 6000 μm.

89. A method for providing a protective and inert coating on carbon steel and stainless steel comprising depositing onto a steel substrate and metallurgically bonding thereto a continuous coating of a MCrAlXSi alloy, where M = nickel, cobalt or iron or mixture thereof and X = yttrium, hafnium, zirconium, lanthanum, scandium or combination thereof, having about 0 to 40 wt% chromium, about 3 to 40 wt% aluminum, about 0 to 35 wt% silicon and up to about 5 wt% X, the balance at least 40 wt% M.

90. A method as claimed in claim 89 in which the coating is deposited by physical vapour deposition, thermal spray, plasma transferred arc, weld overlay, isostatic pressing and by slurry coating.
91. A method as claimed in claim 89 in which the coating is comprised of at least two powders of the constituents of the MCrAlSi partially prealloyed and blended together and are deposited onto the substrate, and heated in a vacuum or an oxygen-free atmosphere to a temperature above 500 to about 1200°C for a time effective to initiate reactive sintering and to metallurgically bond the coating as a continuous impermeable coating to the substrate.

92. A method as claimed in claim 91 in which the coating is deposited in a thickness of about 50 to 6000 μm and in which the MCrAlSi coating comprises essentially about 0 to 20 wt% chromium, about 4 to 20 wt% aluminum, about 5 to 20 wt% silicon, and about 0.25 to 1.5 wt% yttrium, the balance being a minimum 40 wt% nickel.

93. A method as claimed in claim 92 in which the substrate is a high chromium stainless steel having 18 to 38 wt% chromium, 18 to 48 wt% nickel, the balance iron and alloying additives and in which the coating is deposited in a thickness of about 120 to 500 μm.

94. A method as claimed in claim 93 in which the coating is deposited in a thickness of about 150 to 350 μm.

95. A method as claimed in claim 94 in which the coating is aluminized by depositing a layer of aluminum having a thickness up to about 50% of the MCrAlSi coating onto said coating and heat-treating the aluminum layer at a soak temperature in the range of about 1000 to 1160°C for at least 10 minutes effective to establish a multiphased structure.

96. A method as claimed in claim 95 in which the layer of aluminum is deposited in a thickness of about 20% of the MCrAlSi coating by magnetron sputtering physical vapour deposition at a temperature in the range of about 200 to 500°C.

97. A method as claimed in claim 91 in which the substrate, MCrAlYSi coating and aluminum layer are subsequently heated in an oxygen-containing atmosphere at a temperature in the range of 1000 to 1160°C for a time effective to form a layer of α₂-alumina thereon.

98. A method as claimed in claim 91 in which chromium, aluminum and silicon are atomized to form a CrAlSi powder prior to blending with nickel, NiCr or NiAl powders, or combinations thereof.

99. A surface alloyed component produced by the method of claim 89.
100. A surface alloyed component produced by the method of claim 92.
FIG. 6
FIG. 7