

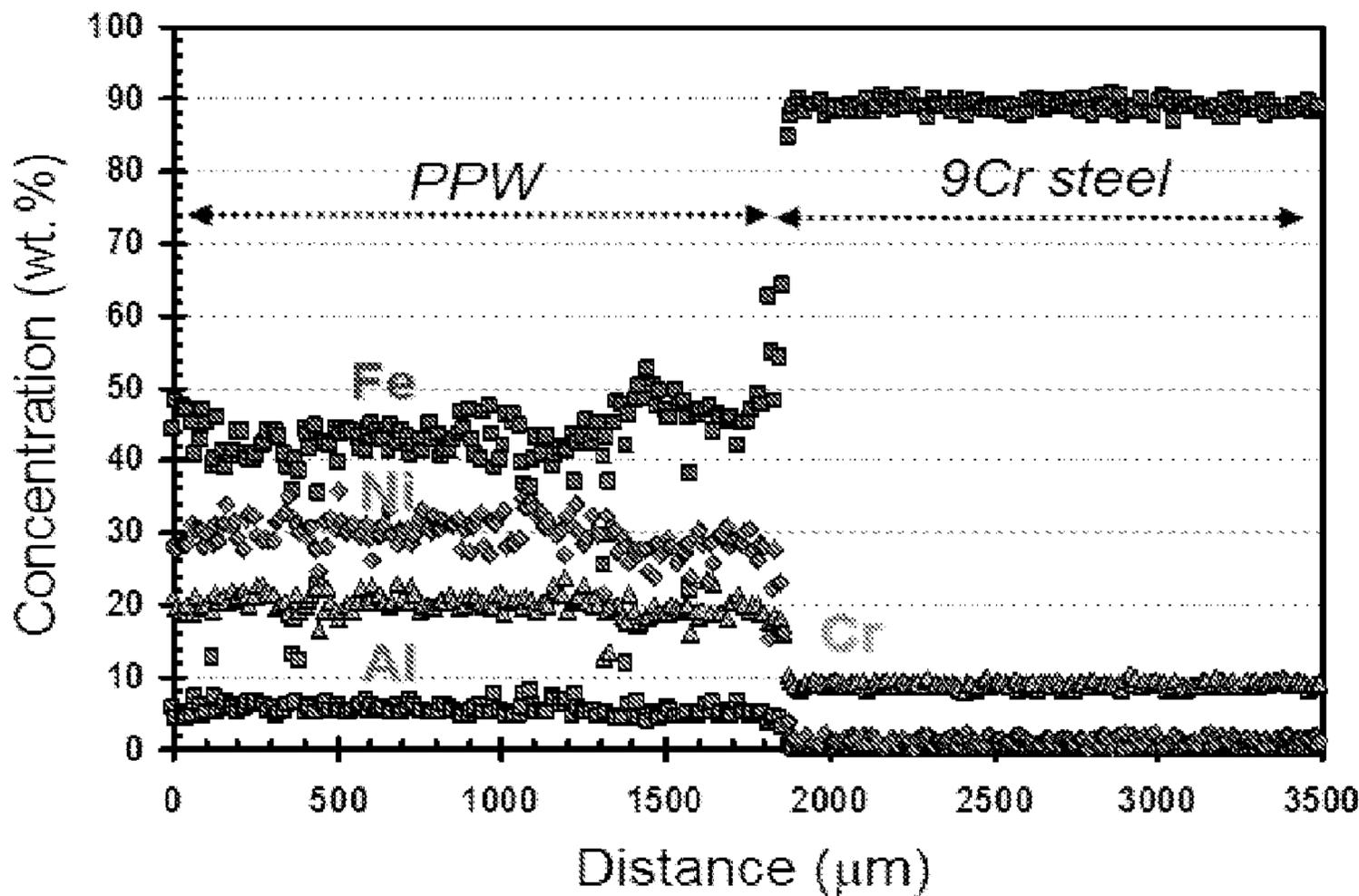


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(54) Titre : TUBE BIMETALLIQUE FORME A PARTIR D'UN ALLIAGE ALUMINOFORMEUR POUR FOURS DE
 RAFFINERIE ET PROCEDE DE FABRICATION ET D'UTILISATION ASSOCIE
 (54) Title: ALUMINA FORMING BIMETALLIC TUBE FOR REFINERY PROCESS FURNACES AND METHOD OF
 MAKING AND USING

FIGURE 2



(57) **Abrégé/Abstract:**

Provided is a bimetallic tube for transport of hydrocarbon feedstocks in refinery process furnaces, and more particularly in furnace radiant coils, including: i) an outer tube layer being formed from carbon steels or low chromium steels comprising less than 15.0



(57) **Abrégé(suite)/Abstract(continued):**

wt.% Cr based on the total weight of the steel; ii) an inner tube layer being formed from- an alumina forming bulk alloy including 5.0 to 10.0 wt.% of Al, 20.0 wt.% to 25.0 wt.% Cr, less than 0.4 wt.% Si, and at least 35.0 wt.% Fe with the balance being Ni, wherein the inner tube layer is formed plasma powder welding the alumina forming bulk alloy on the inner surface of the outer tube layer; and iii) an oxide layer formed on the surface of the inner tube layer.

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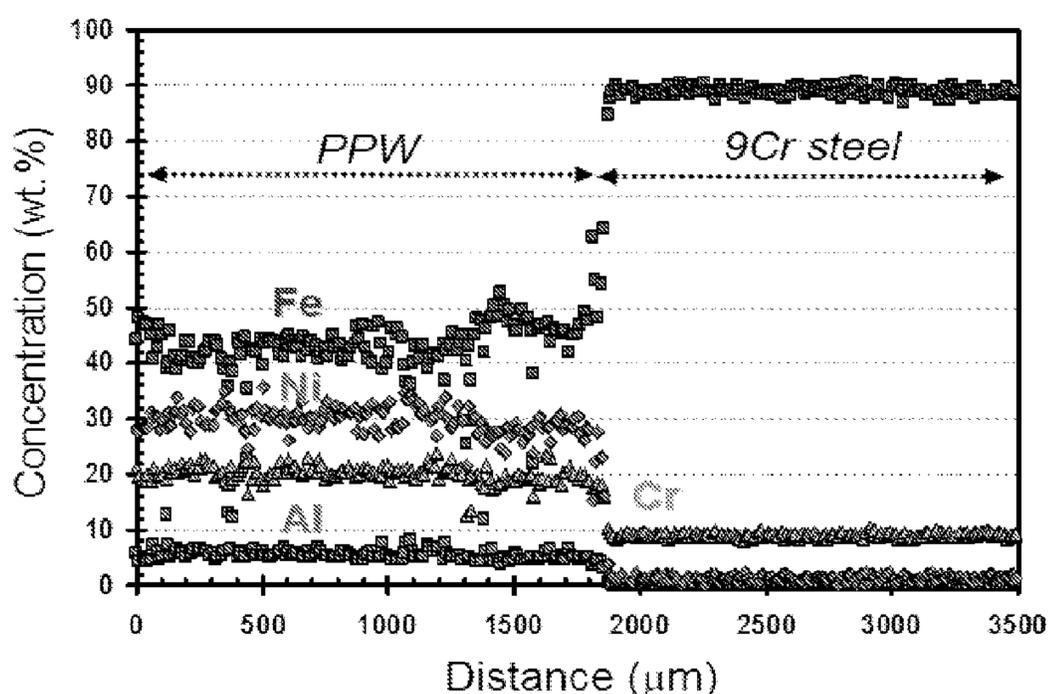
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[Continued on next page]

(54) Title: ALUMINA FORMING BIMETALLIC TUBE FOR REFINERY PROCESS FURNACES AND METHOD OF MAKING AND USING

FIGURE 2



(57) Abstract: Provided is a bimetallic tube for transport of hydrocarbon feedstocks in refinery process furnaces, and more particularly in furnace radiant coils, including: i) an outer tube layer being formed from carbon steels or low chromium steels comprising less than 15.0 wt.% Cr based on the total weight of the steel; ii) an inner tube layer being formed from- an alumina forming bulk alloy including 5.0 to 10.0 wt.% of Al, 20.0 wt.% to 25.0 wt.% Cr, less than 0.4 wt.% Si, and at least 35.0 wt.% Fe with the balance being Ni, wherein the inner tube layer is formed plasma powder welding the alumina forming bulk alloy on the inner surface of the outer tube layer; and iii) an oxide layer formed on the surface of the inner tube layer.

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ALUMINA FORMING BIMETALLIC TUBE FOR REFINERY
PROCESS FURNACES AND METHOD OF MAKING AND USING

FIELD

[001] The present disclosure provides for the composition of, methods of making and methods of using bimetallic tubes for the transport of hydrocarbon feedstocks in refinery process furnaces, and more particularly in furnace radiant coils in order to reduce corrosion, coking and fouling.

BACKGROUND

[002] In typical refinery processes, stored heavy crude oil is cleaned of contaminants (e.g., sand, salts and water) as the first step in the refining process by passage through desalting units. The clean crude feedstock is then heated by passing the desalted crude through a series of heat exchangers. The crude is then passed through a furnace that heats the crude oil to a higher temperature. The furnace, which may be an oil, natural or refinery fuel gas-fired furnace or electrically fired furnaces, heats the oil and is injected into an atmospheric distillation tower. The extreme heat produces physical splitting of the crude oil into combustion gas (furnace fuel gas) and other gaseous light ends, liquid products, and an atmospheric resid fraction.

[003] A large amount of heavy resid content is characteristic of heavy oils. The atmospheric resid must be subjected to more refining. Following the atmospheric tower, the resid is further heated in another series of heat exchangers and then another furnace and sent to a vacuum distillation tower, where light vacuum gas oil and heavy vacuum gas oil are extracted from the resid. The remaining tarry fluid left near the base of the vacuum tower, the vacuum residue, can either be (i) claimed as asphalt, or (ii) subject to further processing, such as

coking. In various coking processes, the resid is heated to high temperatures of 850-950°F (454-510°C) such that the light boiling products are thermally cracked off of the aromatic cores in the resid and are distilled overhead and the solid coke remains.

[004] The delayed coking process is one of the most widely commercially practiced of the coking processes. The resid is heated to the coking temperature by flowing through a long tube in a furnace and then allowed to react at this elevated temperature after flowing into the bottom of a high cylindrical insulated drum. The volatile products are removed to a fractionator and coke accumulates in the drum. The heavy liquid product from the fractionator is recycled back to the furnace. When the drum fills up with coke, the feed is switched to a second drum. The coke is mined out of the drum by drilling a hole down the center with high pressure water and cutting out the remainder also with high-pressure water to get the drum ready for the next coke accumulation cycle.

[005] In Fluid CokingTM, the resid is sprayed onto a hot, fluidized bed of coke particles in a vessel (i.e., the reactor). The volatile products are removed to a fractionator while the coke particles are removed from the bottom of the vessel and transferred to another vessel (i.e., the burner), where the coke is partially burned with air to provide heat for the process. The coke then is recirculated back to the reactor. Since this process produces much more coke than is required for heating the process, fluid coke is withdrawn at the bottom of the reactor.

[006] In FLEXICOKINGTM, a third vessel (i.e., the gasifier), is added to the Fluid Coking process. In the gasifier, coke is gasified with steam and air in net reducing conditions to produce a low BTU gas containing hydrogen, carbon monoxide, nitrogen, and hydrogen sulfide. The hydrogen sulfide is removed using adsorption. The remaining low BTU gas is burned as a clean fuel within the refinery and/or in a nearby power plant.

[007] Visbreaking is a low conversion thermal process used originally to reduce the resid viscosity for heavy fuel oil applications. Today, it often uses a resid that exceeds minimum heavy fuel oil specifications and converts just enough to obtain 15-30% transportation boiling range liquids and still have the heavy product meet heavy fuel oil specifications. Since this process cannot tolerate coke formation, it is required to be within the coke induction period that may limit conversion, rather than heavy fuel oil specifications. A visbreaker reactor may be similar to a delayed coker with a furnace tube followed by a soaker drum. However, the drum is much smaller in volume to limit the residence time with the entire liquid product flowing through. Alternatively, the entire visbreaker may be a long tube coiled within a furnace. Upsets cause coke to form and accumulate on visbreaker walls, which requires periodic decoking.

[008] Refinery process furnaces are widely used to heat hydrocarbon feedstocks in a variety of services, for example, crude oil feed to an atmospheric tower, crude residuum from the atmospheric tower for feed to a vacuum tower, and the like. Perhaps the most severe service is the heating of feedstock to a delayed coker. While coke deposition can be a problem in any refinery process furnace, because of the high temperatures employed and the residual nature of the coker feedstock, there is a pronounced tendency for the formation of coke deposits on the inside wall of the radiant tubing through the coker preheat furnace and the vacuum tower furnace.

[009] Regardless of service, the formation of coke deposits is not desirable. Coke deposits can lead to increased pressure in the tubes due to the restriction of flow, and to higher tube wall temperatures due to the insulative effects of the coke deposits. Both higher pressure and higher temperature lead to premature failure of the tubes. Furthermore, it is often necessary to periodically remove the tube from service and remove the coke deposits by burning off the deposited coke by oxidation with air or another oxidant that is passed through the tube at a high

temperature. This periodic burn-off can result in severe thermal cycling, which also reduces the life of the tube.

[010] The coker tube furnace is the heart of the delayed coking process. The heater furnishes all of the heat in the process. Typically, there are two to four passes per furnace. The tubes are mounted horizontally on the side and held in place with alloy hangers. Multiple burners are along the bottom of the radiant wall opposite from the tubes and are fired vertically upward. Tall furnaces are advantageous since the roof tubes are less likely to have flame impingement and overheating by both radiation and convection. Normally just the radiant section of the heater is used to heat the oil for a delayed coker. The upper convection section of the coker heater is used in some refineries to preheat the oil going to the fractionator or for other uses (e.g., steam generation).

[011] The radiant section tubes in a fired heater used in many refinery process units can experience fouling on the inside and/or outside of the tube surface. External tube fouling occurs when the heater is oil fired. During oil combustion solid particulate matter is formed containing carbon, sulfur and metals which are present in fuel oil. This particulate matter will over time collect on external tube surfaces. Fired heaters that heat crude and reduced crude usually experience the highest level of internal fouling. With these fluids, the fouling occurs due to (i) the presence of solids in the fluid, (ii) thermal cracking forming high molecular weight compounds and (iii) in situ corrosion products. All these materials can end up sticking to the tube wall and forming "coke". Liquids lighter than crude can also form internal deposits. For example, fired heaters heating liquid naphtha can experience internal tube fouling due to corrosion products and/or polymerization reactions forming long chain molecules which stick to the tube wall. Internal tube fouling usually has a large impact on heater operation and thermal efficiency.

[012] These formations/foulant/coke deposits can result in an increase in the radiant tube metal temperature (TMT). As coke forms inside the heater tube, an

insulation barrier between the metal and the “colder” process fluid is formed, resulting in an increased TMT. If coking is allowed to occur without intervention, a tube rupture as a result of high TMT (due to lessened metal strength) is possible. To avoid this, heaters with internal coke deposits can be operated at reduced rates (and hence reduced efficiency and productivity) such that metallurgical constraints are not exceeded on the tubes and tube rupture is avoided. Heaters in fouling service are designed to accommodate a specified TMT increase above the clean tube condition. When that limit is reached steps must be taken to remove the foulant. Often this means the heater must be shut down for cleaning. A secondary effect of internal fouling is increased pressure drop, which limits capacity and throughput. Heaters in fouling service are also designed to accommodate a specified increase in pressure drop. In most cases, the TMT limit is reached before the pressure drop limit. When coke forms in the heater tubes, it insulates the inside of the tube which results in elevated temperatures on the outside of the tube. With good operational practices, coker furnace can be operational for 18 months before decoking of the tubes is needed. Depending on the tube metallurgy, when temperatures approach 1250°F (677°C) on the exterior skin thermocouple, the furnace must be steam spalled and/or steam-air decoked or cooled down and cleaned by hydraulic or mechanical pigging.

[013] During normal use, the internal surfaces of the fired heater tubes are subject to carburization sulfidation, naphthenic acid corrosion and other forms of high temperature corrosion as a result of the prolonged exposure to the stream of heavy crude oil, resid and other petroleum fractions. Carburization is a form of high temperature degradation, which occurs when carbon from the environment diffuses into the metal, usually forming carbides in the matrix and along grain boundaries at temperatures generally in excess of 1000°F (538°C). Carburized material suffers an increase in hardness and often a substantial reduction in toughness, becoming embrittled to the point of exhibiting internal creep damage due to the increased volume of the carbides. Crude oils and hydrocarbon fractions

which contain reactive sulfur are corrosive to carbon and low/medium alloy steels at temperatures above 500°F (260°C) and will cause sulfidation corrosion which forms iron sulfide. This sulfide scale that is formed is often referred to as sulfide induced fouling. Those which contain naphthenic acidic components are corrosive to carbon and low/medium alloy steels at temperatures above 400°F (204°C) and directly remove metal from the surface of the fired heater tube. Corrosion on the internal surfaces of the fired heater tubes creates an uneven surface that can enhance fouling because the various particles found in the petroleum stream may attach themselves to the roughened surface. It is also suggested that corroded surfaces may also provide a “more hospitable” surface for foulant lay down.

[014] The radiant coil of the refinery process furnace has an inlet pipe section and an outlet pipe section. A plurality of essentially straight horizontal pipe sections is arranged in at least two vertical banks. The vertical banks are parallel and horizontally spaced apart. A plurality of bent pipe sweep return bends are arranged in vertical banks at either end of the straight pipe banks. Each bend connects a pair of straight pipe sections in adjacent vertical banks thereof. The return bends are sloped between horizontal and vertical, and one of the straight pipe sections in the pair connected by a return bend is elevated with respect to the other. A tubeside fluid flow path is provided from the inlet pipe section through an alternating series of the straight pipe sections and the return bends to the outlet pipe section. The coil preferably includes first and second vertical straight pipe banks and opposing return bend banks, wherein the straight pipe sections and the return bends are evenly spaced from adjacent sections and bends above and below, except for uppermost and lower most pipe sections and return bends. The return bends at either end of the adjacent tube banks can be oppositely sloped so as to provide a generally horizontal-helical flow pattern. The coil preferably has first and second nested passes, wherein the fluid flow paths of the first and second passes each comprise a series of alternating straight pipe sections in each of said

vertical banks thereof, wherein the straight pipe sections of the first pass in the first and second banks are horizontally spaced opposite the straight pipe sections of the second pass in the respective second and first banks. The first and second pass straight pipe sections in each vertical tube bank can be alternated every other one from top to bottom.

[015] A plurality of essentially straight horizontal radiant coils in the refinery process furnace, more specifically, in the vacuum tower furnace is made out of low chromium steels such as T9 and T5 for enhanced corrosion resistance, creep strength and rupture ductility. The typical composition of radiant coils used in the refinery process furnace is shown in Table 1.

Table 1. Typical composition of radiant coils in the refinery process furnace

Base Metal, R	Alloy	UNS No.	Alloy Compositions (Weight %)
Carbon steels	1018	G10180	Bal.Fe, 0.6-0.9Mn, 0.14-0.20C
	4130	G41300	Bal.Fe, 0.35-0.60Mn, 0.80-1.15Cr, 0.27-0.34C
Low chromium steels	T11	K11562	Bal.Fe:1.25Cr:0.5Mo, 0.5Si, 0.3Mn, 0.15C, 0.045P, 0.045S
	T22	K21590	Bal.Fe:2.25Cr:1.0Mo, 0.5Si, 0.3Mn, 0.15C, 0.035P, 0.035S
	T5	S50100	Bal.Fe:5Cr:0.5Mo, 0.5Si, 0.3Mn, 0.15C, 0.04P, 0.03S
	T9	J82090	Bal.Fe:9Cr:1.0Si, 0.35Mn, 0.02C, 0.04P, 0.045S

[016] All the listed materials for refinery furnace tubes are either carbon steels or low chromium steels that contains chromium less than about 15.0 wt.%, preferably less than about 10.0 wt.%, based on the total weight of the steel. Corrosion protection of these materials relies on protective Cr₂O₃ films on the tube surface. However, chromium concentration in these steels are not sufficient enough to form such a protective film and rather forms a complex corrosion scale comprised of spinel and magnetite type oxide and sulfide. This corrosion scale leads to rough surfaces, high surface areas, and a large number of surface sites for the anchoring of coke and coke precursors.

[017] The listed low chromium steels may contain small amounts of carbide formers such as vanadium, niobium and titanium for precipitation strengthening and/or grain refinement. These alloying elements also affect transformation hardening and weldability of the low chromium steels. The three general types of creep-resistant low chromium steels are Cr-Mo steels, Cr-Mo-V steels and modified Cr-Mo steels. The Cr-Mo steels are widely used in oil refineries, chemical industries and electrical power generating plants for tubing, piping, heat exchangers, super heater tubes, and pressure vessels. The main advantage of these steels is the improved creep strength from Mo and Cr additions and the enhanced corrosion resistance from Cr. The creep strength of Cr-Mo steels is derived mainly from two sources: solid-solution strengthening the ferrite matrix by carbon, molybdenum, and chromium, and precipitation hardening by carbides. Creep strength generally, but not always, increases with higher amounts of Mo and Cr. The effects of Cr and Mo on creep strength are rather complex. For example, T22 steel has higher creep strength than T5 steel.

[018] Synthetic crudes are derived from processing of bitumens, shale, tar sands or extra heavy oils and are also processed in refinery operations. These synthetic crudes present additional fouling problems, as these feedstocks are too heavy and contaminant laden for the typical refinery to process. The materials are often pre-treated at the production site and then shipped to refineries as synthetic crudes. These crudes may contain fine particulate siliceous inorganic matter, such as in the case of tar sands. Some may also contain reactive olefinic materials that are prone to forming polymeric foulant deposits within the fired heater tubes.

[019] Currently, there are various surface modification techniques available for reducing corrosion and fouling in the fired heater tubes for refinery operations. Most of them are based on thin film coatings and include alonizing, hexamethyldisilazane (HMDS) and liquid phase silicate coatings. Alonizing is a diffusion alloying method and applied to the metal surface at elevated

temperatures. As a result, about 100 μ thick, aluminum enriched layer forms on the metal surface. However, this coating, as characteristic of all such relatively thin coatings, reveals poor mechanical integrity and thermal stability due to presence of voids, defects and intermetallic brittle phases in the layer and has low reliability.

[020] Therefore, there is a need to significantly reduce corrosion and fouling in the fired heater tubes in refinery processing operations that does not encounter the drawbacks associated with the current techniques.

SUMMARY

[021] According to the present disclosure, an advantageous bimetallic tube for the transport of hydrocarbon feedstocks through refinery process furnaces, and more particularly the furnace radiant coils, comprises: i) an outer tube layer being formed from carbon steels or low chromium steels comprising less than 15.0 wt.% Cr based on the total weight of the steel; ii) an inner tube layer being formed from an alumina forming bulk alloy comprising 5.0 to 10.0 wt.% of Al, 20.0 wt.% to 25.0 wt.% Cr, less than 0.4 wt.% Si, and at least 35.0 wt.% Fe with the balance being Ni, wherein the inner tube layer is formed by plasma powder welding the alumina forming bulk alloy on the inner surface of the outer tube layer; and iii) an oxide layer formed on the surface of the inner tube layer, wherein the oxide layer comprises alumina, chromia, silica, mullite, spinels, or combinations thereof.

[022] A further aspect of the present disclosure relates to an advantageous bimetallic tube for the transport of hydrocarbon feedstocks through refinery process furnaces, and more particularly the furnace radiant coils, comprising: i) an outer tube layer being formed from carbon steels or low chromium steels comprising less than 10.0 wt.% Cr based on the total weight of the steel, ii) an inner tube layer being formed from an alumina forming bulk alloy comprising 5.0 wt.% to 8.0 wt.% of Al, 20.0 wt.% to 24.0 wt.% Cr, less than 0.3 wt.% Si, and at

least 40.0 wt.% Fe with the balance being Ni, wherein the inner tube layer is formed by plasma powder welding the alumina forming bulk alloy on the inner surface of the outer tube layer; and iii) an oxide layer formed on the surface of the inner tube layer, wherein the oxide layer comprises alumina, chromia, silica, mullite, spinels, or mixtures thereof.

[023] Another aspect of the present disclosure relates to an advantageous method of making a bimetallic tube for the transport of hydrocarbon feedstocks through refinery process furnaces, and more particularly the furnace radiant coils, comprising the steps of : i) providing an outer tube layer, wherein said outer tube layer is formed from carbon steels or low chromium steels comprising less than 15.0 wt.% Cr based on the total weight of the steel; ii) plasma powder welding an inner tube layer on the inner surface of the outer tube layer, wherein the inner tube layer is formed from an alumina forming bulk alloy comprising 5.0 to 10.0 wt.% of Al, 20.0 wt.% to 25.0 wt.% Cr, less than 0.4 wt.% Si, and at least 35.0 wt.% Fe with the balance being Ni; and iii) forming an oxide layer on the surface of the inner tube layer, wherein the oxide layer comprises alumina, chromia, silica, mullite, spinels, or combinations thereof.

[024] A still further aspect of the present disclosure relates to an advantageous method of making a bimetallic tube for the transport of hydrocarbon feedstocks through refinery process furnaces, and more particularly the furnace radiant coils, comprising the steps of: i) providing an outer tube layer being formed from carbon steels or low chromium steels comprising less than 10.0 wt.% Cr based on the total weight of the steel; ii) plasma powder welding an inner tube layer on the inner surface of the outer tube layer, wherein the inner tube layer is formed from an alumina forming bulk alloy comprising 5.0 wt.% to 8.0 wt.% of Al, 20.0 wt.% to 24.0 wt.% Cr, less than 0.3 wt.% Si, and at least 40.0 wt.% Fe with the balance being Ni; and iii) forming an oxide layer on the surface of the

inner tube layer, wherein the oxide layer comprises alumina, chromia, silica, mullite, spinels, or combinations thereof.

[025] A still yet further aspect of the present disclosure relates to an advantageous method of reducing corrosion, coking and/or fouling in refinery process furnaces, and more particularly in the furnace radiant coils for the transport of hydrocarbon feedstocks in refinery process operations comprising: providing bimetallic tubes for the refinery process furnaces, and more particularly in furnace radiant coils, wherein the bimetallic tubes comprise: i) an outer tube layer being formed from carbon steels or low chromium steels comprising less than 15.0 wt.% Cr based on the total weight of the steel; ii) an inner tube layer being formed from an alumina forming bulk alloy comprising 5.0 to 10.0 wt.% of Al, 20.0 wt.% to 25.0 wt.% Cr, less than 0.4 wt.% Si, and at least 35.0 wt.% Fe with the balance being Ni, wherein the inner tube layer is formed by plasma powder welding the alumina forming bulk alloy on the inner surface of the outer tube layer; and iii) an oxide layer formed on the surface of the inner tube layer, wherein the oxide layer comprises alumina, chromia, silica, mullite, spinels, or combinations thereof.

[026] A still yet further aspect of the present disclosure relates to an advantageous method of reducing corrosion, coking and/or fouling in refinery process furnaces, and more particularly in furnace radiant coils for the transport of hydrocarbon feedstocks in refinery process operations comprising: providing bimetallic tubes for refinery process furnaces, and more particularly in furnace radiant coils, wherein the bimetallic tubes comprise: i) an outer tube layer being formed from carbon steels or low chromium steels comprising less than 10.0 wt.% Cr based on the total weight of the steel; ii) an inner tube layer being formed from an alumina forming bulk alloy comprising 5.0 wt.% to 8.0 wt.% of Al, 20.0 wt.% to 24.0 wt.% Cr, less than 0.3 wt.% Si, and at least 40.0 wt.% Fe with the balance being Ni, wherein the inner tube layer is formed by plasma powder welding the

alumina forming bulk alloy on the inner surface of the outer tube layer; and iii) an oxide layer formed on the surface of the inner tube layer, wherein the oxide layer comprises alumina, chromia, silica, mullite, spinels, or combinations thereof.

[027] These and other features and attributes of the disclosed compositions for bimetallic tubes and methods of making and using of the present disclosure and their advantageous applications and/or uses will be apparent from the detailed description which follows, particularly when read in conjunction with the figures appended hereto.

BRIEF DESCRIPTION OF DRAWINGS

[028] To assist those of ordinary skill in the relevant art in making and using the subject matter hereof, reference is made to the appended drawings, wherein:

[029] **Figure 1** depicts a cross-sectional scanning electron microscope (SEM) image of the bimetallic tube revealing the outer 9Cr (T9) steel layer and the inner alumina-forming plasma powder welding (PPW) layer.

[030] **Figure 2** depicts an energy dispersive x-ray spectroscopy (EDXS) concentration line profile of each main element of an alumina-forming bimetallic tube of the present disclosure.

DETAILED DESCRIPTION

[031] All numerical values within the detailed description and the claims herein are modified by “about” or “approximately” the indicated value, and take into account experimental error and variations that would be expected by a person having ordinary skill in the art.

[032] The present disclosure provides compositions of, methods of making and methods of using alumina forming bimetallic tubes for a radiant coil of the refinery process furnace. The present disclosure also provides novel compositions and methods to achieve stable, durable surfaces to resist high temperature corrosion and coking refinery process furnaces, and more particularly in furnace radiant coils, and other components in refinery process furnaces for transporting or conveying hydrocarbon process streams, which may be prone to coking. The present disclosure also provides novel compositions and methods to achieve stable, durable surfaces to resist high temperature corrosion and fouling in fired heater tubes, in refinery process furnaces and other components used for transporting or conveying process streams, which may be prone to fouling.

[033] In one non-limiting exemplary form, the present disclosure provides a bimetallic tubes for the transport of hydrocarbon feedstocks in refinery process furnaces, and more particularly in furnace radiant coils comprising: i) an outer tube layer being formed from carbon steels or low chromium steels comprising less than 15.0 wt.% Cr based on the total weight of the steel; ii) an inner tube layer being formed from an alumina forming bulk alloy comprising 5.0 wt.% to 10.0 wt.% of Al, 20.0 wt.% to 25.0 wt.% Cr, less than 0.4 wt.% Si, and at least 35.0 wt.% Fe with the balance being Ni, wherein an inner tube layer is formed by a PPW process on the inner surface of the outer tube layer; and iii) an oxide layer formed on the surface of the inner tube layer, wherein the oxide layer is substantially comprised of alumina, chromia, silica, mullite, spinels, or mixtures thereof, wherein hydrocarbon feedstocks flow. The oxide layer is advantageously alumina.

[034] In an alternative exemplary form, the present disclosure provides bimetallic tubes for the transport of hydrocarbon feedstocks in refinery process furnaces, and more particularly in furnace radiant coils comprising: i) an outer tube layer being formed from carbon steels or low chromium steels comprising

less than 10.0 wt.% Cr based on the total weight of the steel; ii) an inner tube layer being formed from an alumina forming bulk alloy comprising 5.0 wt.% to 8.0 wt.% of Al, 20.0 wt.% to 24.0 wt.% Cr, less than 0.3 wt.% Si, and at least 40.0 wt.% Fe with the balance being Ni, wherein the inner tube layer is formed by a PPW process on the inner surface of the outer tube layer; and iii) an oxide layer formed on the surface of the inner tube layer, wherein the oxide layer is substantially comprised of alumina, chromia, silica, mullite, spinels, or mixtures thereof, wherein hydrocarbon feedstocks flow.

[035] The bimetallic tubes disclosed herein include an oxide layer, an inner tube layer and an outer tube layer, which are described in detail below.

[036] Oxide Layer

[037] In one form, the oxide layer is a mono-layer or multi-layer and comprised of alumina, chromia, silica, mullite, spinels and mixtures thereof and may contain some impurity oxides formed from the element constituting an alumina forming bulk alloy. One advantageous oxide layer is substantially alumina. The alumina layer advantageously forms from the alumina forming bulk alloy comprising 5.0 wt.% to 10.0 wt.% of Al, 20.0 wt.% to 25.0 wt.% Cr, less than 0.4 wt.% Si, and at least 35.0 wt.% Fe with the balance being Ni, based on the total weight of the alumina forming bulk alloy. The thickness of an oxide layer may range from at least 1 nm to 100 μm , or from at least 10 nm to 50 μm , or from at least 100 nm to 10 μm .

[038] The oxide layer on the surface of the alumina forming bulk alloy forms in-situ during use of the alumina forming bulk alloy when exposed to hydrocarbon process streams in petrochemical or refining process units. Alternatively, the oxide layer on the surface of the alumina forming bulk alloy forms prior to use by exposing the bimetallic tube material to controlled low oxygen partial pressure environments.

[039] In another form, the oxide layer on the surface of the alumina forming bulk alloy described herein may also be formed on the alumina forming bulk alloy by exposing the alumina forming bulk alloy to controlled low oxygen partial pressure environments. The controlled low oxygen partial pressure environments are gaseous environments having thermodynamic oxygen partial pressures less than that of air. Non-limiting examples of a controlled low oxygen partial pressure environment are a refinery or petrochemical plant steam, gaseous H₂O:H₂ mixture and a gaseous CO₂:CO mixture. The controlled low oxygen partial pressure environment may further contain other gases such as CH₄, NH₃, N₂, O₂, He, Ar and hydrocarbons, which may further enable formation of a stable oxide layer comprising alumina, chromia, silica, mullite, spinels, and mixtures thereof on the alumina forming bulk alloy. Therefore, the protective oxide layer may be formed prior to exposure of the alumina forming bulk alloy to hydrocarbon process streams in petrochemical and refinery process units. Non-limiting exemplary temperature ranges of the controlled low oxygen partial pressure environment may be from 500°C to 1200°C, or from 600°C to 1100°C. Non-limiting exemplary exposure times may range from 1 hour to 500 hours, or from 1 hour to 300 hours, or from 1 hour to 100 hours.

[040] Inner Tube Layer

[041] In one form, the alumina forming bulk alloy comprises 5.0 wt.% to 10.0 wt.% of Al, 20.0 wt.% to 25.0 wt.% Cr, less than 0.4 wt.% Si, and at least 35.0 wt.% Fe. The alumina forming bulk alloy compositions of the present disclosure offers significant advantages relative to prior art alloy compositions for use as the bimetallic tube to mitigate corrosion and coking of the fired heater tubes when exposed to hydrocarbon streams in refining process furnaces. In particular, it was unexpectedly found that both Fe and Cr contents in combination with Si in the alumina-forming bulk alloy composition are beneficial to fabricate a crack-free bimetallic tube with carbon steels or low chromium steels comprising less than

15.0 wt.% Cr, or less than 10.0 wt.% Cr, or less than 7.5 wt.% Cr, or less than 5.0 wt.% Cr based on the total weight of the steel.

[042] In one form, the alumina forming bulk alloy comprises at least 35.0 wt.% iron, or at least 40.0 wt.% iron, or at least 43.0 wt.% iron, or at least 46.0 wt.% iron based on the total weight of the alumina forming bulk alloy. Presence of iron in the alumina forming bulk alloy provides improved thermal and mechanical compatibility with carbon steels or low chromium steels to fabricate crack-free bimetallic tube of the instant disclosure. As chromium content decreases in carbon steels or low chromium steels, iron content in the alumina forming bulk alloy needs to be increased. As a non-limiting example, iron content in the alumina forming bulk alloy is at least 35.0 wt.% for 9Cr (T9) steel to fabricate crack-free bimetallic tube of the instant disclosure. As another non-limiting example, iron content in the alumina forming bulk alloy is at least 40.0 wt.% for 5Cr (T5) steel to fabricate crack-free bimetallic tube of the instant disclosure. As yet another non-limiting example, iron content in the alumina forming bulk alloy is preferably at least 43.0 wt.% for 2.25Cr (T22) or 1.25Cr (T11) steels to fabricate crack-free bimetallic tube of the instant disclosure. The higher iron content in the alumina forming bulk alloy provides improved thermal and mechanical compatibility with low chromium steels to fabricate crack-free bimetallic tube of the instant disclosure.

[043] The alumina forming bulk alloy includes 5.0 wt.% to 10.0 wt.% aluminum, or 5.0 wt.% to 9.0 wt.% aluminum, or 5.0 wt.% to 8.0 wt.% aluminum. The alumina forming bulk alloy further includes 20.0 wt.% to 25.0 wt.% chromium, or 20.0 wt.% to 24.0 wt.% chromium, or 20.0 wt.% to 23.0 wt.% chromium. The alumina forming bulk alloy may also include less than 0.4 wt.% silicon, or less than 0.3 wt.% silicon, or less than 0.25 wt.% silicon. Excessive amounts of silicon (e.g., greater than 0.5 wt.% silicon) in the alumina forming bulk alloy may promote solidification-induced cracking on carbon steels or low

chromium steels when it is formed by plasma powder welding method. In one form, the alumina forming bulk alloy may include less than 0.1 wt.% carbon, or less than 0.08 wt.% carbon, or less than 0.05 wt.% carbon. Carbon can be present in the alumina forming bulk alloy as a form of carbide precipitates, which provide creep strength of the alumina forming bulk alloy when it is exposed to high temperatures for extended periods of time.

[044] Alloying elements, such as for example, Ga, Ge, As, In, Sn, Sb, Pb, Pd, Pt, Cu, Ag and Au, provide reduced coking because these elements are non-catalytic to surface carbon transfer reaction. Alloying elements, such as for example, Re, Ru, Rh, Ir, Pd, Pt, Cu, Ag and Au, provide increased coating integrity, stability and durability and provide a defect-free alumina layer when it forms from the alumina forming bulk alloy including 5.0 wt.% to 10.0 wt.% of Al, 20.0 wt.% to 25.0 wt.% Cr, less than 0.4 wt.% Si, and at least 35.0 wt.% Fe with the balance being Ni. In one form, the alumina forming bulk alloy disclosed herein includes 0.1 wt.% to 2.0 wt.% of at least one element selected from Ga, Ge, As, In, Sn, Sb, Pb, Pd, Pt, Cu, Ag, Au and combinations thereof. In another form, the alumina forming bulk alloy disclosed herein includes 0.1 wt.% to 2.0 wt.% of at least one element chosen from Re, Ru, Rh, Ir, Pd, Pt, Cu, Ag, Au and combinations thereof.

[045] The alumina forming bulk alloy may further include 0.01 wt.% to 2.0 wt.% of at least one element chosen from Sc, La, Y, Ce and combinations thereof. In yet another form, the alumina forming bulk alloy may include 35.0 wt.% iron, 6.0 wt.% aluminum, 22.0 wt.% chromium, and 0.5 wt.% yttrium with the balance being Ni. In still another form, the alumina forming bulk alloy includes 40.0 wt.% iron, 5.5 wt.% aluminum, 21.0 wt.% chromium, and 0.3 wt.% yttrium with the balance being Ni. The alumina forming bulk alloy may further include 0.01 wt.% to 2.0 wt.% of oxide particles of at least one element chosen from Al, Si, Sc, La, Y, Ce and combinations thereof. In yet another form, the alumina forming

bulk alloy includes 35.0 wt.% iron, 6.0 wt.% aluminum, 22.0 wt.% chromium, and 0.5 wt.% Y_2O_3 with the balance being Ni. In still yet another form, the alumina forming bulk alloy includes 40.0 wt.% iron, 5.5 wt.% aluminum, 21.0 wt.% chromium, and 0.3 wt.% Y_2O_3 with the balance being Ni. The alumina forming bulk alloy may further include 0.01 wt.% to 4.0 wt.% of at least one element chosen from Mn, Ti, Zr, Hf, V, Nb, Ta, Mo, W, and combinations thereof. The foregoing elements provide precipitation strengthening and/or grain refinement and affect transformation hardening and weldability of the alumina forming bulk alloy when it is formed by plasma powder welding method.

[046] In one advantageous form, the alumina forming bulk alloy includes 0.34 wt.% Si, 20.70 wt.% Cr, 5.66 wt.% Al, 41.40 wt.% Fe with the balance being Ni. In yet another advantageous form, the alumina forming bulk alloy includes 0.17 wt.% Si, 21.28 wt.% Cr, 5.67 wt.% Al, 41.55 wt.% Fe with the balance being Ni. In yet another advantageous form, the alumina forming bulk alloy includes 0.20 wt.% Si, 22.10 wt.% Cr, 6.90 wt.% Al, 36.30 wt.% Fe with the balance being Ni. In another advantageous form, the alumina forming bulk alloy includes 5.0 wt.% to 10.0 wt.% of Al, 20.0 wt.% to 25.0 wt.% Cr, less than 0.4 wt.% Si, and at least 35.0 wt.% Fe with the balance being Ni. In still yet another advantageous form, the alumina forming bulk alloy includes 5.0 wt.% to 8.0 wt.% of Al, 20.0 wt.% to 24.0 wt.% Cr, less than 0.3 wt.% Si, and at least 40.0 wt.% Fe with the balance being Ni.

[047] The alumina forming bulk alloy may further include intermetallic precipitates at from 0.1 wt.% to 30.0 wt.%, including, but not limited to, Ni_3Al , $NiAl$ and sigma-phase. The alumina forming bulk alloy may further include inclusions at from 0.01 wt.% to 5.0 wt.%, including, but not limited to, oxide, carbide, nitride and carbonitride inclusions. These intermetallic precipitates and inclusions are formed from the constituting elements of the alumina forming bulk alloy including, but not limited to, Fe, Ni, Cr, Al and Si. Both intermetallic

precipitates and oxide, carbide, nitride and carbonitride inclusions may provide improved high temperature creep strength.

[048] The alumina forming bulk alloy of the present disclosure has a low porosity, which contributes to its improved resistance to corrosion and coking when exposed to hydrocarbon feedstocks in refinery process furnaces, and more particularly in furnace radiant coils. The alumina forming bulk alloy has less than 2.0 vol.% porosity, or less than 1.0 vol.% porosity, or less than 0.5 vol.% porosity, or less than 0.1 vol.% porosity. Excessive porosity in the alumina forming bulk alloy serves as a pathway for gaseous molecules of hydrocarbon feedstocks in refinery process furnaces to transfer gaseous molecules to the alumina forming bulk alloy interior. The transfer of gaseous molecules triggers corrosion in the alumina forming bulk alloy and deterioration of mechanical strength. Thus, it is advantageous to achieve an alumina forming bulk alloy including a minimal amount of porosity.

[049] In one advantageous form, the low porosity of the alumina forming bulk alloy may be formed by a powder plasma welding (PPW) method. PPW is not a coating technology like thermal spraying, but a welding overlay technology. With PPW, metal powder is melted and welded by plasma torch on the inside surface of the base tube. A metal overlay having a thickness of 1.0 to 3.0 mm, 1.5 to 2.5 mm, or 1.75 to 2.25 mm is strongly bonded to base tube and provides the almost pore-free layer. The alumina forming bulk alloy may be optionally post-annealed, tempered, laser melted or a combination thereof to achieve a higher density material.

[050] In contrast, the conventional thermal spray coating processes such as plasma, HVOF and detonation gun generally yield a coating metal layer that is of a higher porosity. The conventional thermal spray coating is produced by a process in which molten or softened particles are applied by impact onto a substrate. The coating often contains reticular or lamellar grain structure resulting

from the rapid solidification of small globules, flattened from striking a cold surface at high velocities. It is difficult to ensure that all particles are the exact same size and achieve the same temperature and velocity. Thus, variations in the conditions of the individual particles on impact during thermal spray process lead to heterogeneous structure, which includes excessive porosity.

[051] In accordance with one aspect of the present disclosure, the interior surface of the wall of the fired heater tubes being formed from an alumina forming bulk alloy disclosed herein may have an average surface roughness (Ra) of less than 40 micro inches (1.1 μm), or less than 20 micro inches (0.5 μm), or less than 10 micro inches (0.25 μm). In various forms, the inner surfaces of the plurality of the fired heater tubes disclosed herein may have the above-mentioned surface roughness. Such a surface roughness may further reduce coking. The smooth surface within the inner diameter of the fired heater tubes may reduce coking of the hydrocarbon feedstocks flowing through the tubes.

[052] Exemplary non-limiting means of reducing the surface roughness may include mechanical polishing, electro polishing, lapping and combinations thereof. There are additional benefits of reducing the surface roughness of the coated metal. One of the benefits is the shifting from a linear growth rate of the foulant, which results in the continuous thickening of the foulant deposit; to an asymptotic growth rate which reaches a finite thickness and then stops thickening.

[053] Outer Tube Layer

[054] In accordance with another aspect of the present disclosure, the outer tube layer of the alumina-forming bimetallic tube may be formed from carbon steels or low chromium steels that contains chromium at less than 15.0 wt.%, or less than 10.0 wt.%, or less than 7.5 wt.%, or less than 5.0 wt.%, based on the total weight of the steel. One advantageous outer tube layer is formed from low chromium steels. Non-limiting examples of such a low chromium steel include

T11, T22, T5 and T9 as listed in Table 1. Thus, the alumina forming bulk alloy of the instant disclosure may be applied to the interior surface of the low chromium steel by a PPW method in order to ensure low porosity and crack-free metallurgical bonding. During use or prior to exposure to hydrocarbon feedstocks, a protective alumina layer forms on the surface of the alumina forming bulk alloy, which provides corrosion and coking resistance.

[055] Other Exemplary Embodiments

[056] Thus, the present disclosure provides a bimetallic tube for use in refinery process furnaces, and more particularly in furnace radiant coils, including: i) an outer tube layer being formed from carbon steels or low chromium steels comprising less than 15.0 wt.% Cr based on the total weight of the steel; ii) an inner tube layer being formed from an alumina forming bulk alloy comprising 5.0 to 10.0 wt.% of Al, 20.0 wt.% to 25.0 wt.% Cr, less than 0.4 wt.% Si, and at least 35.0 wt.% Fe with the balance being Ni, wherein an inner tube layer is formed by a PPW process on the inner surface of the outer tube layer; and iii) an oxide layer formed on the surface of the inner tube layer, wherein the oxide layer is substantially comprised of alumina, chromia, silica, mullite, spinels, or mixtures thereof, wherein hydrocarbon feedstocks flow.

[057] In an alternative form, the present disclosure also provides a bimetallic tube for use in refinery process furnaces, and more particularly in furnace radiant coils, including: i) an outer tube layer being formed from carbon steels or low chromium steels comprising less than 10.0 wt.% Cr based on the total weight of the steel, ii) an inner tube layer being formed from an alumina forming bulk alloy comprising 5.0 wt.% to 8.0 wt.% of Al, 20.0 wt.% to 24.0 wt.% Cr, less than 0.3 wt.% Si, and at least 40.0 wt.% Fe with the balance being Ni, wherein the inner tube layer is formed by a PPW process on the inner surface of the outer tube layer; and iii) an oxide layer formed on the surface of the inner tube layer, wherein the

oxide layer is substantially comprised of alumina, chromia, silica, mullite, spinels, or mixtures thereof, wherein hydrocarbon feedstocks flow.

[058] The present disclosure also provides a method for reducing corrosion, coking and/or fouling in refinery process furnaces, and more particularly in furnace radiant coils for the transport of hydrocarbon feedstocks in refinery process operations. The method provides a bimetallic tube for use in the refinery process furnaces, and more particularly in furnace radiant coils, including: i) an outer tube layer being formed from carbon steels or low chromium steels comprising less than 15.0 wt.% Cr based on the total weight of the steel; ii) an inner tube layer being formed from an alumina forming bulk alloy comprising 5.0 to 10.0 wt.% of Al, 20.0 wt.% to 25.0 wt.% Cr, less than 0.4 wt.% Si, and at least 35.0 wt.% Fe with the balance being Ni, wherein an inner tube layer is formed by a PPW process on the inner surface of the outer tube layer; and iii) an oxide layer formed on the surface of the inner tube layer, wherein the oxide layer is substantially comprised of alumina, chromia, silica, mullite, spinels, or mixtures thereof, wherein hydrocarbon feedstocks flow.

[059] In an alternative form, a method for reducing corrosion, coking and/or fouling in refinery process furnaces, and more particularly in furnace radiant coils for the transport of hydrocarbon feedstocks in refinery process operations includes providing a bimetallic tube for use in the refinery process furnaces, and more particularly in furnace radiant coils comprising: i) an outer tube layer being formed from carbon steels or low chromium steels comprising less than 10.0 wt.% Cr based on the total weight of the steel; ii) an inner tube layer being formed from an alumina forming bulk alloy comprising 5.0 to 8.0 wt.% of Al, 20.0 wt.% to 24.0 wt.% Cr, less than 0.3 wt.% Si, and at least 40.0 wt.% Fe with the balance being Ni, wherein the inner tube layer is formed by a PPW process on the inner surface of the outer tube layer; and iii) an oxide layer formed on the surface of the inner tube layer, wherein the oxide layer is substantially comprised of alumina,

chromia, silica, mullite, spinels, or mixtures thereof, wherein hydrocarbon feedstocks flow.

[060] The present disclosure also provides a method of making a bimetallic tube for the transport of hydrocarbon feedstocks in refinery process furnaces, and more particularly in furnace radiant coils, including the steps of: i) providing an outer tube layer, wherein said outer tube layer is formed from carbon steels or low chromium steels comprising less than 15.0 wt.% Cr based on the total weight of the steel; ii) plasma powder welding an inner tube layer on the inner surface of the outer tube layer, wherein the inner tube layer is formed from an alumina forming bulk alloy comprising 5.0 to 10.0 wt.% of Al, 20.0 wt.% to 25.0 wt.% Cr, less than 0.4 wt.% Si, and at least 35.0 wt.% Fe with the balance being Ni; and iii) forming an oxide layer on the surface of the inner tube layer, wherein the oxide layer comprises alumina, chromia, silica, mullite, spinels, or combinations thereof.

[061] In an alternative form, a method of making a bimetallic tube for the transport of hydrocarbon feedstocks in refinery process furnaces, and more particularly in furnace radiant coils, includes the steps of: i) providing an outer tube layer being formed from carbon steels or low chromium steels comprising less than 10.0 wt.% Cr based on the total weight of the steel; ii) plasma powder welding an inner tube layer on the inner surface of the outer tube layer, wherein the inner tube layer is formed from an alumina forming bulk alloy comprising 5.0 to 8.0 wt.% of Al, 20.0 wt.% to 24.0 wt.% Cr, less than 0.3 wt.% Si, and at least 40.0 wt.% Fe with the balance being Ni; and iii) forming an oxide layer on the surface of the inner tube layer, wherein the oxide layer comprises alumina, chromia, silica, mullite, spinels, or combinations thereof.

[062] Advantages and Applications

[063] Metal surfaces to reduce corrosion, fouling and coking of the fired heater tubes exposed to hydrocarbon feedstocks in refinery process furnaces, and more particularly in furnace radiant coils may be constructed of the alumina forming bulk alloy disclosed herein.

[064] The advantages of the disclosed bimetallic tubes of the present disclosure include, *inter alia*, one or more of reduced corrosion and/or reduced fouling in the fired heater tubes in refinery processing operations and reduced corrosion and/or reduced coking in the fired heater tubes in refinery process furnace operations. More particularly, the advantages of the compositions disclosed herein include, but are not limited to, a reduction of carburization and sulfidation corrosion and the reduction of coking in fired heater tubes in refining processing facilities, refinery process furnaces, more particularly in furnace radiant coils, and in other ancillary and related industries such as synthetic fuels processes (e.g., coal to liquids, coal gasification and gas to liquids) and other components used for transporting or conveying hydrocarbon process feedstocks, which may be prone to corrosion and coking. The present disclosure also relates to the reduction of corrosion and coking associated with process streams, which include, but are not limited to hydrocarbon feedstock streams encountered in refinery process furnaces. It more particularly relates to methods of reducing corrosion and coking in fired heater tubes in refinery process furnaces by use of alumina forming bimetallic tube.

[065] The bimetallic tubes of the present disclosure described herein may be utilized in the following non-limiting types of applications and uses. Surfaces of the fired heater tubes which would benefit from the alumina forming bulk alloy of the instant disclosure include apparatus, reactor systems and units that are in contact with hydrocarbon process streams at any time during use. In refining process applications, these apparatus, reactor systems and units include, but are

not limited to, atmospheric and vacuum distillation pipestills, cokers and visbreakers in refinery processing facilities and other components used for transporting or conveying process streams, which may be prone to corrosion and fouling. In petrochemical process applications, these apparatus, reactor systems and units include, but are not limited to, radiant coil, convection coil and transfer line exchangers (TLEs) in steam cracker furnaces and other components used for transporting or conveying hydrocarbon process streams, which may be prone to corrosion and coking.

TEST METHODS

[066] Chemical composition may be determined by electron probe micro-analyzer (EPMA). EPMA is fundamentally the same as scanning electron microscopy (SEM) with the added capability of chemical analysis. The primary importance of EPMA is the ability to acquire precise, quantitative elemental analyses by wavelength dispersive spectroscopy (WDS). The spatial scale of analysis, combined with the ability to create detailed images of the sample, makes it possible to analyze materials in situ and to resolve complex chemical variation within single phases. Alternatively chemical composition may be determined by energy dispersive x-ray spectroscopy (EDXS).

[067] Roughness is routinely expressed as the arithmetic average roughness (Ra). The arithmetic average height of roughness component of irregularities from the mean line is measured within the sample length L. The standard cut-off is 0.8 mm with a measuring length of 4.8 mm. This measurement conforms to ANSI/ASME B46.1 "Surface Texture – Surface Roughness, Waviness and Lay", which was employed in determining the surface roughness in accordance with the present disclosure.

[068] The following are examples of the present disclosure and are not to be construed as limiting.

EXAMPLES

[069] Example 1: Crack-free alumina-forming bimetallic tube made out of 9Cr (T9) low chromium steel.

[070] A small segment of the 9Cr (T9) furnace tube in the size of 5.00" OD x 4.25" ID x 12.0" L was prepared and the interior surface of the tube was machined for the PPW process. The alumina forming PPW powder "M" was prepared via argon gas atomization method. The powder was sieved to a certain size to enable easy flow during the PPW process. The chemical composition of the powder "M" was Balanced Ni:22.93Cr:6.68Al:33.76Fe:0.36Si in wt.%. The bimetallic tube was fabricated by applying the powder "M" onto the interior surface of 9Cr furnace tube via the PPW method.

[071] The resultant bimetallic tube was comprised of: i) a 9.5 mm thick outer tube layer of T9 low chromium steel; ii) a 2.0 mm thick inner tube layer being formed from an alumina forming bulk alloy; and iii) a 50 nm thick native alumina film formed on the surface of the inner tube layer. The cross sectional image of the bimetallic tube revealing the outer 9Cr steel layer and the inner alumina-forming PPW layer is shown in Figure 1.

[072] The chemical composition of alumina forming bulk alloy determined by EPMA was Balanced Ni:20.70Cr:5.66Al:41.40Fe:0.34Si in wt.%. Since Si concentration was less than 0.4 wt.%, Fe concentration was at least 35.0 wt.%, and Cr concentration was 20.0 wt.% to 25.0 wt.%, a crack-free alumina-forming bimetallic tube was fabricated. Detailed microscopic examination by use of SEM revealed columnar grain structure of the inner tube layer being formed from an alumina forming bulk alloy by a PPW process. Also observed in the microstructure were Al-rich Ni₃Al or NiAl type grains, aluminum nitride inclusions and Cr-rich carbide precipitates. Figure 2 shows an EDXS concentration line profile of each main element of an alumina-forming bimetallic

tube of the present invention. The inner tube layer being formed from an alumina forming bulk alloy (marked as PPW) shows about 6 wt.% Al, 21 wt.% Cr, and 42 wt.% Fe with the balance being Ni. EDXS is not as accurate as EPMA, but still provides a result that the inner tube layer being formed from an alumina forming bulk alloy is comprised of 5.0 to 10.0 wt.% of Al, 20.0 wt.% to 25.0 wt.% Cr, less than 0.4 wt.% Si, and at least 35.0 wt.% Fe with the balance being Ni. Scattering of each data point is due to presence of intermetallic precipitates, Cr-rich carbide precipitates, and aluminum nitride inclusions in the PPW layer.

[073] Example 2: Crack-free alumina-forming bimetallic tube made out of 9Cr (T9) low chromium steel.

[074] A small segment of the 9Cr (T9) furnace tube in the size of 5.00" OD x 4.25" ID x 12.0" L was prepared and the interior surface of the tube was machined for the PPW process. The alumina forming PPW powder "O" was prepared via argon gas atomization method. The powder was sieved to a certain size to enable easy flow during the PPW process. The chemical composition of the powder "O" was Balanced Ni:24.20Cr:6.25Al:32.20Fe:0.14Si in wt.%. The bimetallic tube was fabricated by applying the powder "O" onto the interior surface of 9Cr furnace tube via the PPW method.

[075] The resultant bimetallic tube was comprised of: i) a 9.5 mm thick outer tube layer of T9 low chromium steel; ii) a 2.0 mm thick inner tube layer being formed from an alumina forming bulk alloy; and iii) a 50 nm thick native alumina film formed on the surface of the inner tube layer. The cross sectional image of the bimetallic tube revealing the outer 9Cr steel layer and the inner alumina-forming PPW layer is shown in Figure 1.

[076] The chemical composition of alumina forming bulk alloy determined by EPMA was Balanced Ni:21.28Cr:5.67Al:41.55Fe:0.17Si in wt.%. Since Si concentration was less than 0.3 wt.%, Fe concentration was at least 40.0 wt.%,

and Cr concentration was 20.0 wt.% to 24.0 wt.%, a crack-free alumina-forming bimetallic tube was fabricated. Detailed microscopic examination by use of SEM revealed columnar grain structure of the inner tube layer being formed from an alumina forming bulk alloy by a PPW process. Also observed in the microstructure were Al-rich Ni₃Al or NiAl type grains, aluminum nitride inclusions and Cr-rich carbide precipitates.

[077] Example 3 (Comparative Example): Cracked alumina-forming bimetallic tube made out of 9Cr (T9) low chromium steel.

[078] A small segment of the 9Cr (T9) furnace tube in the size of 5.00" OD x 4.25" ID x 12.0" L was prepared and the interior surface of the tube was machined for the PPW process. The alumina forming PPW powder "N" was prepared via argon gas atomization method. The powder was sieved to a certain size to enable easy flow during the PPW process. The chemical composition of the powder "N" was Balanced Ni:19.82Cr:7.36Al:39.30Fe:0.25Si in wt.%. The bimetallic tube was fabricated by applying the powder "N" onto the interior surface of 9Cr furnace tube via the PPW method.

[079] The resultant bimetallic tube was comprised of: i) a 9.5 mm thick outer tube layer of T9 low chromium steel; ii) a 2.0 mm thick inner tube layer being formed from an alumina forming bulk alloy; and iii) a 50 nm thick native alumina film formed on the surface of the inner tube layer. The cross sectional image of the bimetallic tube revealing the outer 9Cr steel layer and the inner alumina-forming PPW layer is shown in Figure 1.

[080] The chemical composition of alumina forming bulk alloy determined by EPMA was Balanced Ni:17.07Cr:5.04Al:39.48Fe:0.21Si in wt.%. Although Si concentration was less than 0.3 wt.%, Fe concentration was less than 40.0 wt.% and Cr concentration was also less than 20.0 wt.%. Due to lower amount of Fe and Cr, the resultant alumina forming bimetallic tube revealed "blow hole"

crack-like defects after standard penetration test. This result confirms that although Si concentration was less than 0.3 wt.% in the alumina-forming PPW layer both Fe and Cr concentration should be at least 40 wt.% and 20 wt.%, respectively to fabricate the crack-free bimetallic tube of this disclosure.

[081] Example 4: Crack-free alumina-forming bimetallic tube made out of 9Cr (T9) low chromium steel.

[082] A small segment of the 9Cr (T9) furnace tube in the size of 5.00" OD x 4.25" ID x 12.0" L was prepared and the interior surface of the tube was machined for the PPW process. The alumina forming PPW powder "N+O" was prepared via argon gas atomization method. The powder was sieved to a certain size to enable easy flow during the PPW process. The chemical composition of the powder "N+O" was Balanced Ni:22.01Cr:6.81Al:35.75Fe:0.22Si in wt.%. The bimetallic tube was fabricated by applying the powder "N+O" onto the interior surface of 9Cr furnace tube via the PPW method.

[083] The resultant bimetallic tube was comprised of: i) a 9.5 mm thick outer tube layer of T9 low chromium steel; ii) a 2.0 mm thick inner tube layer being formed from an alumina forming bulk alloy; and iii) a 50 nm thick native alumina film formed on the surface of the inner tube layer. The cross sectional image of the bimetallic tube revealing the outer 9Cr steel layer and the inner alumina-forming PPW layer is shown in Figure 1.

[084] The chemical composition of alumina forming bulk alloy determined by EPMA was Balanced Ni:22.10Cr:6.90Al:36.30Fe:0.20Si in wt.%. Since Si concentration was less than 0.4 wt.%, Fe concentration was at least 35.0 wt.%, and Cr concentration was 20.0 wt.% to 24.0 wt.%, a crack-free alumina-forming bimetallic tube was fabricated. Detailed microscopic examination by use of SEM revealed columnar grain structure of the inner tube layer being formed from an alumina forming bulk alloy by a PPW process. Also observed in the

microstructure were Al-rich Ni₃Al or NiAl type grains, aluminum nitride inclusions and Cr-rich carbide precipitates.

[085] Applicants have attempted to disclose all embodiments and applications of the disclosed subject matter that could be reasonably foreseen. However, there may be unforeseeable, insubstantial modifications that remain as equivalents. While the present invention has been described in conjunction with specific, exemplary embodiments thereof, it is evident that many alterations, modifications, and variations will be apparent to those skilled in the art in light of the foregoing description without departing from the spirit or scope of the present disclosure. Accordingly, the present disclosure is intended to embrace all such alterations, modifications, and variations of the above detailed description.

[086] All patents, test procedures, and other documents cited herein, including priority documents, are fully incorporated by reference to the extent such disclosure is not inconsistent with this invention and for all jurisdictions in which such incorporation is permitted.

[087] When numerical lower limits and numerical upper limits are listed herein, ranges from any lower limit to any upper limit are contemplated.

CLAIMS:

1. A bimetallic tube for the transport of hydrocarbon feedstocks through the radiant coils of refinery process furnaces, comprising: i) an outer tube layer being formed from carbon steels or low chromium steels comprising less than 15.0 wt.% Cr based on the total weight of the steel; ii) an inner tube layer being formed from an alumina forming bulk alloy comprising 5.0 to 10.0 wt.% of Al, 20.0 wt.% to 25.0 wt.% Cr, less than 0.4 wt.% Si, and at least 35.0 wt.% Fe with the balance being Ni, wherein the inner tube layer is formed by plasma powder welding the alumina forming bulk alloy on the inner surface of the outer tube layer; and iii) an oxide layer formed on the surface of the inner tube layer, wherein the oxide layer comprises alumina, chromia, silica, mullite, spinels, or combinations thereof.
2. The bimetallic tube of claim 1, wherein the outer tube layer is a low chromium steel chosen from T11, T22, T5 and T9 steels.
3. The bimetallic tube of any one of the preceding claims, wherein the inner tube layer further comprises less than 0.01 wt.% carbon.
4. The bimetallic tube of any one of the preceding claims, wherein the inner tube layer further comprises 0.1 wt.% to 2.0 wt.% of at least one element chosen from Ga, Ge, As, In, Sn, Sb, Pb, Pd, Pt, Cu, Ag, Au and combinations thereof.
5. The bimetallic tube of any one of the preceding claims, wherein the inner tube layer further comprises 0.1 wt.% to 2.0 wt.% of at least one element chosen from Re, Ru, Rh, Ir, Pd, Pt, Cu, Ag, Au and combinations thereof.

6. The bimetallic tube of any one of the preceding claims, wherein the inner tube layer further comprises 0.01 wt.% to 2.0 wt.% of at least one element chosen from Sc, La, Y, Ce and combinations thereof.

7. The bimetallic tube of any one of the preceding claims, wherein the inner tube layer further comprises 0.01 wt.% to 2.0 wt.% of oxide particles of at least one element chosen from Al, Si, Sc, La, Y, Ce and combinations thereof.

8. The bimetallic tube of any one of the preceding claims, wherein the inner tube layer further comprises 0.01 wt.% to 4.0 wt.% of at least one element chosen from Mn, Ti, Zr, Hf, V, Nb, Ta, Mo, W, and combinations thereof.

9. The bimetallic tube of any one of the preceding claims, wherein the inner tube layer further comprises 0.1 wt.% to 30.0 wt.% of at least one intermetallic precipitate chosen from Ni_3Al , NiAl , sigma-phase, and combinations thereof.

10. The bimetallic tube of any one of the preceding claims, wherein the inner tube layer further comprises 0.01 wt.% to 5.0 wt.% of at least one inclusion chosen from an oxide, a carbide, a nitride, a carbonitride, and combinations thereof.

11. A method of making a bimetallic tube for the transport of hydrocarbon feedstocks through the radiant coils of refinery process furnaces comprising the steps of: i) providing an outer tube layer, wherein said outer tube layer is formed from carbon steels or low chromium steels comprising less than 15.0 wt.% Cr based on the total weight of the steel; ii) plasma powder welding an inner tube layer on the inner surface of the outer tube layer, wherein the inner tube layer is formed from an alumina forming bulk alloy comprising 5.0 to 10.0 wt.% of Al, 20.0 wt.% to 25.0 wt.% Cr, less than 0.4 wt.% Si, and at least 35.0 wt.% Fe with the balance being Ni; and iii) forming an oxide layer on the surface of the

inner tube layer, wherein the oxide layer comprises alumina, chromia, silica, mullite, spinels, or combinations thereof.

12. The method of claim 11, wherein the forming of the oxide layer on the surface of the inner tube layer occurs in-situ during use of the alumina forming bulk alloy when exposed to hydrocarbon process streams in petrochemical or refining process units.

13. The method of claim 11, wherein the forming of the oxide layer on the surface of the inner tube layer occurs prior to use by exposing the bimetallic tube material to a controlled low oxygen partial pressure environment.

14. The method of claim 13, wherein the controlled low oxygen partial pressure environment is chosen from refinery plant steam, petrochemical plant steam, a gaseous $H_2O:H_2$ mixture, and a gaseous $CO_2:CO$ mixture.

15. The method of claim 13 or 14, wherein the controlled low oxygen partial pressure environment further includes one or more other gases chosen from CH_4 , NH_3 , N_2 , O_2 , He, Ar, hydrocarbons and combinations thereof.

16. The method of claim 13, 14 or 15, wherein the controlled low oxygen partial pressure environment temperature is from $500^\circ C$ to $1200^\circ C$, and wherein the controlled low oxygen partial pressure environment exposure time is from 1 hour to 500 hours.

17. The method of any one of claims 11-16 further including densifying the inner tube layer by a method chosen from post-annealing, tempering, laser melting and combinations thereof.

18. The method of any one of claims 11-17 further including reducing the surface roughness of the inner tube layer by a method chosen from mechanical polishing, electro polishing, lapping and combinations thereof.

19. A method of reducing corrosion, coking and/or fouling from the transport of hydrocarbon feedstocks through the radiant coils of refinery process furnaces comprising: providing bimetallic tubes for the radiant coils of refinery process furnaces, wherein the bimetallic tubes comprise: i) an outer tube layer being formed from carbon steels or low chromium steels comprising less than 15.0 wt.% Cr based on the total weight of the steel; ii) an inner tube layer being formed from an alumina forming bulk alloy comprising 5.0 to 10.0 wt.% of Al, 20.0 wt.% to 25.0 wt.% Cr, less than 0.4 wt.% Si, and at least 35.0 wt.% Fe with the balance being Ni, wherein the inner tube layer is formed by plasma powder welding the alumina forming bulk alloy on the inner surface of the outer tube layer; and iii) an oxide layer formed on the surface of the inner tube layer, wherein the oxide layer comprises alumina, chromia, silica, mullite, spinels, or combinations thereof.

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FIGURE 1

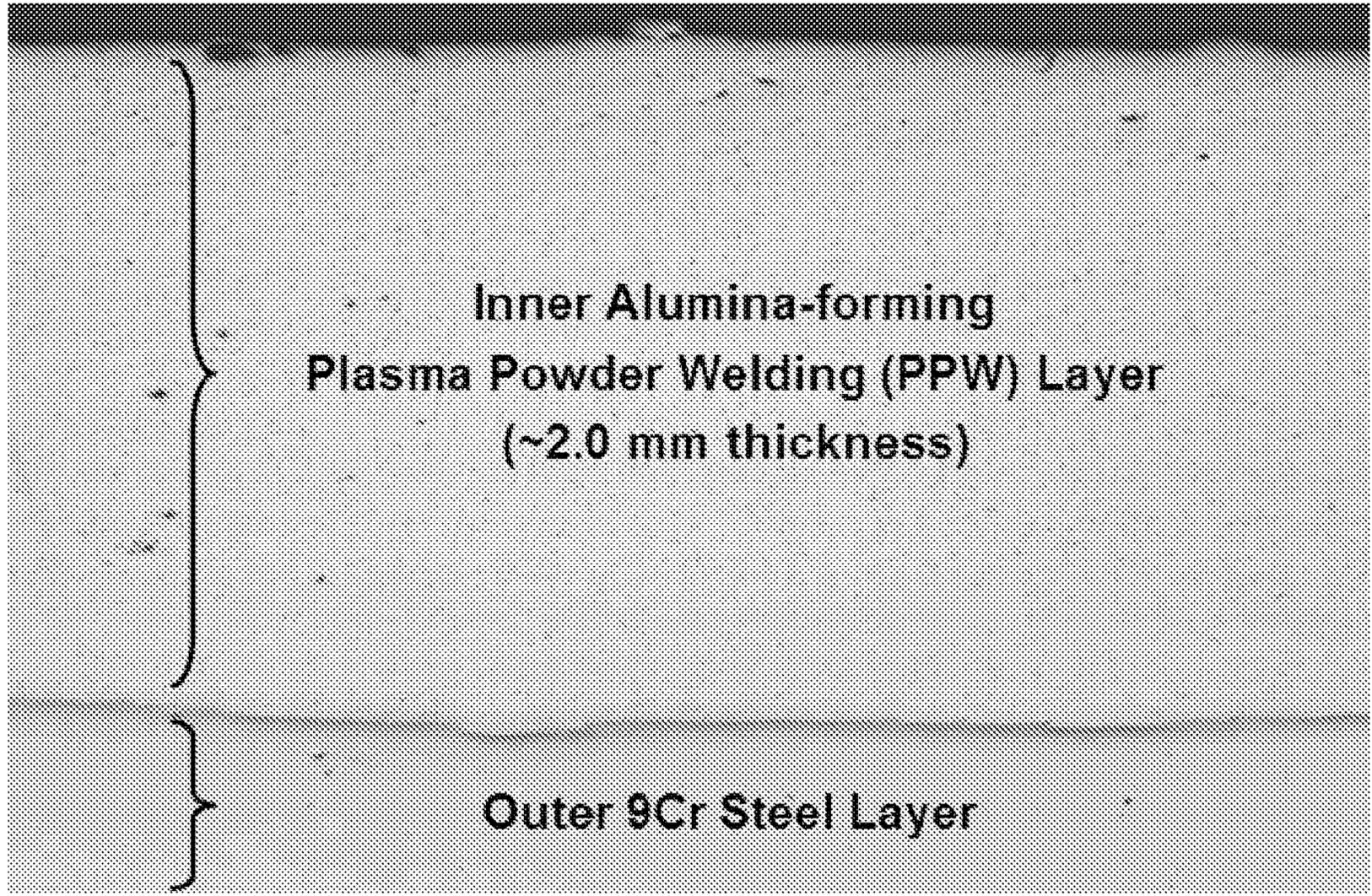


FIGURE 2

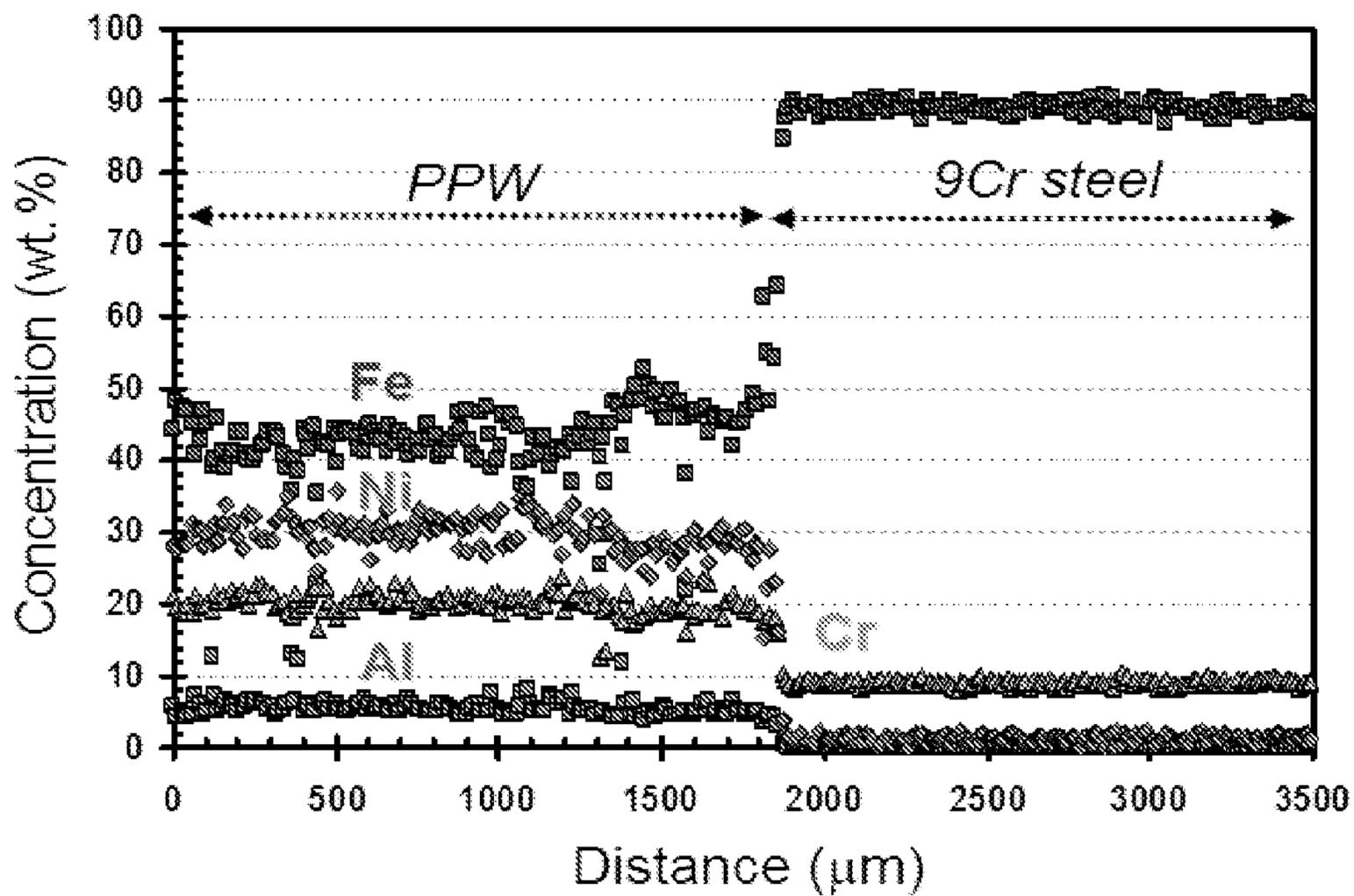


FIGURE 2

