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(54) OXIDATION RESISTENT ALLOY

OXIDATIONSBESTÄNDIGE LEGIERUNG

ALLIAGE RÉSISTANT À L'OXYDATION

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Description

[0001] The present invention relates to alloys used to prepare steel pipes i.e. tubes for use in chemical engineering applications. In particular, the invention relates to low carbon aluminium steel alloys and pipes made from such alloys. They may be used in plant such as ethylene cracker furnaces that need to be able to withstand elevated temperatures for extended periods of time.

[0002] Frequently alloy materials for use at high temperatures, for example, alloy tubes used in ethylene pyrolysis cracker furnaces and to some extent steam methane reforming, suffer from insufficient oxidation and carburisation resistance. The industry continues to look for improved materials and other technologies to enable more efficient ethylene production under increasingly severe pyrolysis/cracking conditions (higher temperatures, shorter residence times, and lower partial pressures of product), leading to increased ethylene yields. Current alloys have specific issues related to their corrosion resistance which causes failure at increasingly high design process temperatures. This is the case currently for both castable alloy tubes and wrought alloy tubes.

[0003] It is necessary to heat the tubes to very high temperatures (above 900°C) to allow the steam cracking to take place continuously. This places stringent design requirements on the reactor and on the pipes used in its construction. A particular problem concerns oxidation and/or corrosion of the pipes as well as problems caused by coking of the pipes during use.

[0004] Pipes for steam cracker furnaces can be prepared by a centrifugal casting process. Centrifugal casting is a well-established process that is used to cast thin-walled cylinders, pipes and other axially symmetric objects. One benefit of this process is that it allows precise control of the metallurgy and crystal structure of the alloy product. It is generally used for casting iron, steel, stainless steels and alloys of aluminium, copper and nickel. The centrifugal casting process employs a permanent mould which is rotated about its axis at high speeds of typically 300 to 3000 rpm as the molten metal is poured. The molten metal is centrifugally thrown towards the inside mould wall where it is able to solidify after cooling. The resulting cast cylinder i.e. tube, has a fine grain and the surface roughness of the outer surface of the cylinder is relatively low.

[0005] JP64-031931 describes the production of a curved tube made of heat-resistant alloy. The tube is prepared by centrifugal casting and the alloy of JP64-031931 is made from high strength and heat-resistant cast steel containing 15 to 30% chromium, 20 to 40% nickel as well as the optional inclusion of smaller quantities of manganese and molybdenum. Small quantities of niobium and titanium are also added to the alloy. The cast tube is then subjected to the further step of an aging treatment at a temperature of from 700 to 1100°C to deposit secondary carbide within the grain structure. This patent does not attempt to control the primary carbide formation or to control the relative amounts of niobium and titanium, or carbon and nitrogen. Subsequently it is subjected to another processing step involving high frequency bending or die-bending at a temperature in the range of 550 to 1100°C.

[0006] WO2012/121389 discloses an alloy intended for use in nuclear applications such as in heat exchanges in pressurised water reactors. The material is said to have excellent thin workability and corrosion resistance. This material is based on a nickel-chromiumiron alloy and contains small amounts of manganese, titanium, and optionally aluminium as alloying elements.

[0007] WO2000/22068 discloses anti-coking coatings for refractory alloys used in the oil industry. The coatings are obtained by a method which involves submitting the refractory alloys surface to the action of oxygen and/or nitrogen gas plasma at low frequency and depositing on the treated surface coating based on silicon oxide, nitride or Oxy nitride by plasma enhanced chemical vapour deposition at low frequency.

[0008] US 2002192494 discloses a method for protecting low-carbon steel and stainless steel from coking and corrosion at elevated temperatures in corrosive environments such as during ethylene production by pyrolysis of hydrocarbons. The coating is an alloy of chromium, aluminium and silicon together with three other components one of which is selected from nickel, cobalt, iron or a mixture of these elements, the second of which is selected from yttrium, hafnium, zirconium, lanthanum, scandium or a combination of those elements, and the third is selected from tantalum, titanium, platinum, palladium, rhenium, molybdenum, tungsten, niobium, boron or a combination of those elements. The blended powder composition of this alloys applied to the surface and heat treated to bond the coating to the surface.

[0009] US 2001001399 discloses austenitic nickel-chromium steel alloys based on steel which are particularly suitable for use as heat resistance and high strength materials for parts, such as pipes, in petrochemical cracking furnaces which are intended for the production of ethylene or synthesis gas. The alloy is a low carbon steel containing from 0.3 to 1.0% carbon

[0010] In addition to all of the usual technical issues associated with preparing a steel pipe for use in chemical plant, there are two particular problems which need to be addressed when fabricating pipes for this type of application. These issues arise because of the harsh working environment that the steel tubes will be exposed to and the fact that any ’downtime’ in plant operation is very costly in terms of lost production. The pipes need to be resistant to oxidation and/or corrosion during extended periods of use. The pipes also need to be capable of being in service for extended periods of time without coking or fouling. De-coking of reactor tubes is traditionally performed by passing air and steam through the pipes to burn the coke. However, this is at least a one or two day operation and therefore results in significant downtime and lost production with the attendant costs of this downtime.

[0011] The present invention aims to provide pipes which are resistant to oxidation. In addition the invention aims for the surfaces of these pipes to be resistant to coke formation with the intention of reducing the frequency of de-coking operations. It is an aim of the invention that when the alloy is made into pipes the surface of these have a superior resistance to coke formation compared with conventional pipes. Similarly, it is an aim of the invention that once formed into pipes and employed in a chemical reactor or similar environment that the surface of the pipes are stable and resistant to chemical attack or oxidation or corrosion etc. In addition, it is an aim of the invention that the pipes should also to have the appropriate mechanical properties in terms of creep resistance and ductility etc. as existing pipes so that they are suitable for use in high-temperature chemical reactors.

[0012] It is also an aim of the present invention to prepare a pipe which can be produced in a process which is convenient to run, so that the manufacturing process is relatively straight forward. It is also an aim to provide a process which is applicable to the large scale production of steel alloy pipes. The invention aims to provide a more economic production method and/or which is also more economic when the whole of life use and maintenance interruptions are considered. It is also an aim of the present invention to provide a steel alloy which is economical to manufacture and which avoids or reduces the need for expensive alloying components.

[0013] It is also an aim to have pipes which can be prepared without the need for further subsequent processing steps.

[0014] The invention satisfies some or all of the above aims.

[0015] According to a first aspect of the present invention, there is provided an alloy comprising:

from 0.15 to 0.35 wt% carbon,
from 2.5 to 5.0 wt% aluminium,
from 40 to 45 wt% nickel,
from 25 to 35 wt% chromium,
from 0.50 to 1.50 wt% niobium and / or vanadium,
from 0.01 wt% to 0.25 wt% yttrium,
from 0.01 wt% to 0.25 wt% tungsten and / or tantalum,
from 0.01 wt% to 0.25 wt% in total of one or more of titanium and / or zirconium and / or hafnium,
up to 0.9 wt% manganese,
up to 0.9 wt% silicon, and
up to 0.10 wt% nitrogen,
with the balance of the composition being iron and incidental impurities.

[0016] In an embodiment, the alloy comprises:

from 0.15 to 0.35 wt% carbon,
from 2.5 to 5.0 wt% aluminium,
from 40 to 45 wt% nickel,
from 25 to 35 wt% chromium,
from 0.50 to 1.50 wt% niobium and / or vanadium,
from 0.01 wt% to 0.05 wt% yttrium,
from 0.05 wt% to 0.25 wt% tungsten and / or tantalum,
from 0.04 wt% to 0.15 wt% in total of one or more of titanium and / or zirconium and / or hafnium,
an amount of up to 0.9 wt% manganese,
an amount of up to 0.6 wt% silicon, and
an amount of up to 0.10 wt% nitrogen,
with the balance of the composition being iron and incidental impurities.

[0017] The alloys of the invention may be used to fabricate steel pipes, particularly steel pipes which are intended to be used in chemical engineering applications such as chemical reactors and ethylene crackers.

[0018] It is the careful control of the metallurgical composition which gives contributes to the improved anti-coking properties of these alloys. Each of the elemental components described in the above steel compositions plays an important role in the properties of the steel and its resistance to coking and oxidation. Without wishing to be bound by theory, we believe that the particular combination of elements gives rise to the superior properties of the alloys of the invention because of the formation of a thin but continuous layer of alumina which is able to form on the surface of the alloy at an early stage in use. This layer is stable and contributes to a reduced level of coke formation because alumina is effectively non-catalytic and does not promote the formation of carbon deposits on the surface. On the contrary, the alumina layer which is formed in use generally provides an environment which is unfavourable to the deposition of carbon on the surface of the pipes.

[0019] In addition, because of the particular chemical composition of the alloys of the invention it is possible for this protective oxide layer to form under what would be considered to be very reducing conditions such as in situ in ethylene cracker. Indeed, the alloys of the present invention are able to form a stable protective surface layer even at partial pressures of oxygen as low as 10^{-27} atmospheres. This means that pipes made from alloys of the invention can be put into use directly without the need for further treatment and without any additional coatings being required. Hence a further benefit of the steel pipes of the invention (i.e. pipes made using steel alloys of the invention) is that they require no subsequent treating after production in order to be used in chemical engineering applications. This is a significant advantage both in terms of time and cost relative to pipes made from existing alloys.

[0020] The alloys of the invention also benefit from the fact that they contain little or no nickel, chromium or iron at the interface of alloy surface / cracking gas. These elements ordinarily behave as catalytic elements when in contact with the cracking gas and would promote coke formation and deposition under normal conditions of use. The ability of the alloys of the present invention to be able during service to avoid any concentration of or the full presence of these elements on its surface and to form an alumina oxide layer containing little or none of these elements represents a substantial advantage relative to prior art alloys. The retention of these particular elements, which would otherwise be problematic in terms of carbon deposition, within the bulk matrix of the alloy is therefore an important feature of the alloys of the present invention and arises as a result of the carefully controlled metallurgy. It can therefore be seen that the combination of the thin surface layer of alumina and the absence of elemental components such as nickel, chromium and iron at the surface together lead to substantial improvements in resistance to coking, coke formation and deposition.

[0021] Surprisingly, the relative proportions of the elements required to secure the anti-coking effect do not adversely affect the mechanical properties of the alloys. This is important because good mechanical properties are required of components in chemical engineering applications. The inventors of surprisingly found that the combination of elements used in the alloys of the present invention also contributes to the high-temperature strength of the steel tube.

[0022] The individual elemental components in the alloy perform the roles discussed below.

CARBON

[0023] Carbon is required in an amount of 0.15 to 0.35 wt.% in the alloys of the invention. The amount is carefully controlled because carbon has several different functions. For example, carbon is usually an important component of steel for providing tensile strength and resistance to creep rupture. This is because carbon is an essential component in the formation of carbides which normally provide steel with its strength due to the precipitation of the primary and secondary carbides. At the same time, the interplay between the amount of aluminium which is added and the amount of carbon must be closely controlled. Aluminium is generally incompatible with carbon as aluminium rejects carbon in the sense of decreasing its solubility in the austenitic matrix. This has the effect of the carbon migrating to the grain boundaries during solidification with the consequence that the alloy precipitates an excessive quantity of primary chromium carbide, forming a thick network that makes it become brittle. Accordingly, it is necessary to have sufficient carbon in the alloy to ensure sufficient strength in the resulting alloy and this is the reason for the requirement to have 0.15 wt% or more carbon in the alloy. At the same time it is important to ensure that the upper limit of the amount of carbon is not too high so that it adversely interacts with the added aluminium. For this reason, the upper limit of carbon is 0.35 wt%. In a preferred embodiment, the amount of carbon is from 0.20 to 0.35%, and in a more preferred embodiment the amount of carbon is from 0.25 to 0.30 wt%.

ALUMINIUM

[0024] Aluminium is another very important component of the alloys of the invention. Aluminium is present in an amount of from 2.5 to 5.0 wt%. Aluminium alloys are generally difficult to cast and therefore can be hard and difficult work. The steels of the present invention are relatively easy to work despite the presence of aluminium.

[0025] Aluminium is necessary for the formation of the alumina protective layer at the surface. At the same time aluminium and carbon compete for solubility and this can be a problem. Furthermore, as mentioned above, aluminium also decreases the solubility of carbon but reciprocally the carbon decreases the solubility of the aluminium in the matrix leading to brittleness. Not only because of the precipitation of thick chromium carbide in the grain boundary during solidification, but also because of the possibility of precipitating in addition thick nickel-aluminide intermetallic. Indeed, the aluminium been rejected like the carbon during solidification too by the austenitic matrix. This involves the undesirable nickel-aluminide precipitation, known for its embrittlement properties, during solidification.

[0026] It is therefore important to ensure that the upper limit of aluminium does not exceed 5 wt% so that the alloy does not become brittle forming uncontrolled excess nickel aluminide intermetallic at the inter-dentric space and grain boundaries. At the same time, a minimum amount of aluminium of 2.5wt% is required in order to ensure that a substantially continuous coating of alumina on the surface of the alloy can be formed in use.

[0027] The aluminium is therefore added to the alloy to allow the formation of a thin protective continuous dense homogenous and adherent alumina (aluminium oxide) layer on the surface of the alloy during service. This aluminium oxide layer is oxidation resistant (slow growth of the oxide layer during service prevents further reaction or oxidation of the alloy). The aluminium oxide is a surface stable barrier stopping the diffusion of carbon in the alloy. It serves to facilitate anti-coking (no catalytic reaction involving formation of graphite/coke during cracking), protecting the alloy, and allows its surface to be case neutral when exposed to the gas to be cracked.

[0028] The higher the aluminium content, the higher the reservoir/stock of aluminium which is important in case the aluminium oxide layer needs to be re-formed. Conditions under which this might be an issue include alumimum oxide spallation due to over-decoking, or variation in the service conditions, or an uncontrolled event in the cracking furnace. The alumina also provides carburisation resistance as described above and hence it is important to ensure that there is sufficient aluminium in the alloy to provide an effective layer. This is the reason for the lower limit of aluminium which is specified. The minimum of 2.5wt wt% is important to ensure the formation of the layer at an appropriate rate during service.

[0029] In the case of the alloys of the present invention, the aluminium content can exceed the usual levels that are normally included in aluminium steels specifically because of the deliberately low level of carbon that is added to the alloys of the invention. It is therefore possible for the amount of aluminium of reach levels much greater than 3.5wt.% because of the relatively low content of carbon with amounts of aluminium up to 5.0wt% being achievable without damaging the properties of the alloy. Above this level there is a risk of the alloy becoming brittle such that for example it can break during manipulation or during following steps of manufacture like pipe straightening after casting.

[0030] The aluminium content is preferably in the range from 3.0 wt% to 5.0 wt%, and more preferably is in the range from 3.2 wt% to 4.6 wt%, such as in the range 3.5 wt% to 4.5 wt%.

[0031] It is important to note that the maximum and minimum aluminium content is considered relative to the carbon content. This is also relevant to the increase of thermal expansion of the alloy at high temperature. The relative proportions of carbon and aluminium, calculated in terms of their wt% in the alloy, ranges from about 1 : 33.3 to 1 : 7.1. Preferably, the relative amounts lie in the range of from about 1 : 17 to 1 : 22.

CHROMIUM

[0032] Chromium is present in an amount of from 25 wt% to 35 wt%. The chromium forms a primary carbide network during solidification (as described in the case of carbon) which give primary strength to the alloy, and also forms secondary carbides during service with good creep resistance properties. In the situation in which the aluminium has been fully depleted after long service of the alloy, or following dramatic decoking of the furnace, the chromium will be able to form an oxide layer which will be able to delay the carburisation of the alloy. The chromium content of the matrix is able to delay carbonisation/carburisation of the alloy by trapping the carbon when it is in the process of diffusing thereby forming chromium carbides.

[0033] Chromium is not anti-coking but provides a well-documented and effective corrosion resistance and oxidation resistance effect in addition to acting as a carbide-former. Carbide formation ensures creep strengthening precipitations in the alloy. The lower limit of 25 wt% of chromium is required in order to ensure sufficient oxidation resistance and the upper limit of 35 wt% is determined by the fact that above this level it is difficult to obtain a stable austenite phase. In addition, too high a level of chromium renders the steel unworkable. In some embodiments, the chromium is present in the range of from 26 wt% to 31 wt%, more particularly in the range of from 28 wt% to 31 wt%, such as in the range 28wt% to 30 wt%. In certain cases, the amount of chromium is in the range from 29 wt% to 30 wt%. In some alternative embodiments, the chromium is present in the range of from 30 wt% to 33 wt%, and more preferably in the range of from 31 wt% to 32 wt%.

[0034] The chromium content is determined in balance with the nickel content for the alloy so that the ultimate alloy possesses a stable austenitic base matrix at elevated temperature. It is important that there is a stable austenitic matrix at every expected service temperature to which the alloy is likely to be exposed. It is therefore important to consider the amount of chromium to be used in the context of the amount of nickel that is also present in the alloy. The relatively high quantity of chromium is intended to provide its availability to form chromium oxide on the surface and to allow chromium to trap carbon in the form of chromium carbide in case of carburisation not contained by the thin alumina oxide.

NICKEL

[0035] Nickel is present in an amount of from 40 wt% to 45 wt%. The nickel provides the stable austenitic matrix base of the alloy. Nickel is an element which is essential in order to obtain a stable austenite structure and improves the stability of austenite and supresses the generation of the sigma phase. Nickel is the austenitic stabiliser element, allowing the alloy to be generally strong at above 800C. Therefore it forms a stable matrix with the iron which allows the possible precipitation of the carbides/nitrides. The lower limit of the nickel content is chosen simply for the reason that this is a sufficient amount for improving the stability of austenite with respect to the lower limits of the other elements.

[0036] Nickel is also very important for cracking furnace applications as it give better carburisation resistance to the alloy, because of its slow carbon diffusion kinetics. In this respect, the kinetics of nickel in terms of carburisation are much slower than in the case of iron. On the other hand, nickel can in some circumstances be deleterious because it promotes the formation of catalytic coke when present in the surface of the alloy, and more precisely at the interface alloy / cracking gas. Thus, the upper limit of nickel is required in order to contribute to the carburisation resistance of the alloy but at the same time should not be exceeded because of its known property to promote catalytic coking if it appears on the surface of the alloy. It is therefore important to ensure that not too much nickel is present in the alloy. In addition, nickel is an expensive material and consequently avoiding to hire nickel content also has an economic advantage. The lower limit of nickel is governed by the need to provide an adequate austenitic matrix. In some embodiments, the nickel is present in an amount of from 42 wt% to 45 wt%, and more preferably in an amount of from 42 wt% to 44 wt%. In some particularly preferred embodiments, the nickel is present in an amount of from 42.5 wt% to 43.5 wt%.

[0037] In some alternative embodiments of the invention, it is possible to replace part of the nickel content by cobalt. Cobalt is able to perform the same function as nickel in the alloys of the invention. In such embodiments, the total amount of cobalt and nickel is from 40 wt% to 45 wt%. Up to 75 wt% of the nickel can be replaced by cobalt, and in principle any amount from 1 wt% to 75 wt% of the nickel can be replaced by cobalt; however, in practice it is more usual for between 5 wt% and 15 wt% of the nickel to be replaced by cobalt on account of the higher cost of cobalt. The quantity of nickel (and cobalt, when present) that is included in the alloy of the present invention is carefully controlled relative to the amount of chromium which is present in order to ensure that the alloy is indeed a stable austenitic matrix at whatever service temperature is employed.

NIOBIUM

[0038] Niobium is present in an amount of from 0.50 to 1.50 wt%. The function of the niobium is to form thin primary carbides during solidification, these primary carbides have the particularity in this specific alloy to re-dissolve at high temperature (therefore during service) and as a consequence to facilitate the precipitation of secondary carbides and ensure their dispersion. This contributes to the creep resistance of the alloy.

[0039] The primary niobium carbides therefore act a reservoir of carbon, which can then be released at the service temperature to create more creep efficient carbides. This role is essential, as the Carbon is not in the usual excess that would be typical in a high-temperature alloy having a carbon content above 0.40wt.%. In the alloys of the present invention, the release of carbon by the niobium compensates for this and therefore provides carbon when it is required. In addition, during solidification the niobium carbides mainly forms at the interdendritic space or grain boundary thereby participating predominantly in the primary carbides network. The amount of niobium employed is chosen on the grounds of its efficiency at disrupting the primary chromium carbide network. In some embodiments, the niobium is present in an amount of from 0.80 wt% to 1.10 wt%, and preferably from 0.80 wt% to 0.90 wt% or from 0.90 wt% to 1.10 wt%. In other embodiments, the niobium is present in an amount of from 1.10 wt.% to 1.30 wt. %.

[0040] In some alternative embodiments of the invention, it is possible to substitute the niobium with vanadium. Vanadium is a carbide former from the same periodic group as niobium and can be employed in the same amounts as described above for niobium. In addition, a mixture of the two can be employed subject to satisfying the ranges mentioned above for niobium for the mixture.

TITANIUM, ZIRCONIUM and HAFNIUM

[0041] Titanium and / or zirconium may be present independently of one another in a total amount of 0.01 wt% to 0.25 wt%, and preferably in an amount of from 0.04 wt% to 0.15 wt%. In other words, titanium can be present within the range stated, with no zirconium being present; or zirconium can be present within the range stated, with no titanium being present; or both titanium and zirconium can be present and in this case each may be present in any amount within the range stated, subject to not exceeding the total limit. Both elements function in a similar manner by forming carbides. It is generally preferred to have titanium present. In some embodiments, the amount of the element or elements (usually but not necessarily only titanium) is from 0.08 wt% to 0.15 wt%, and more preferably is from 0.08 wt% to 0.13 wt%. In some embodiments, only titanium is present in this amount and there is substantially no zirconium or hafnium present.

[0042] Titanium and zirconium are stable carbide-forming elements and are used either singly or together to improve the creep properties of the alloy. Either element individually or both elements together do this by precipitating secondary carbides during service. Furthermore, as carbide forming elements they not only form their respective carbides but also are able to form a titanium / zirconium-niobium double carbide precipitates which improves creep strength.

[0043] In addition, titanium and zirconium have a second function in that they are very active scavengers for oxygen and consequently they help to protect the aluminium present in the melt from oxidation. These elements are therefore oxidised in preference to the aluminium. Titanium / zirconium are added to melt as a deoxidiser.

[0044] The quantities of one or both elements that is / are used represents a balance between obtaining an improvement in the creep properties of the alloy (which decrease due to the addition of aluminium) and undesirable oxide, carbides, nitrides formation when too much is added. Indeed, the addition of too high an amount of titanium or zirconium can lead to the undesirable formation of oxide, carbide, nitride, hardening too much the alloy.

[0045] Cost is also an issue since both of these elements are expensive raw materials.

[0046] In some alternative embodiments of the invention, it is possible to substitute either or both amounts of titanium and zirconium with hafnium.

[0047] Thus, in certain embodiments of the invention hafnium can be employed in addition to or in place of one or both of titanium and zirconium. In other words, in some embodiments of the invention there may be no titanium or zirconium present in the alloy and hafnium is present instead of these elements. In other embodiments, some or all of the titanium and / or zirconium is replaced by hafnium, with the consequence that all three elements are present. In this circumstance, the minimum amount of all three elements together would be 0.04 wt% and the maximum amount of all three elements together would be 0.15 wt%. Hafnium is effective at increasing the creep resistance properties of the alloy but has the disadvantage of being an expensive raw material.

[0048] In certain embodiments of the invention, it is preferable that titanium is used in the alloys of the invention without zirconium or hafnium being present. In an alternative embodiment of the invention, both titanium and zirconium can be used without hafnium being present.

TUNGSTEN

[0049] Tungsten is present in an amount of from 0.01 wt% to 0.25 wt%, and is preferably present in an amount of from 0.05 wt% to 0.25 wt%. Tungsten is a large element in terms of its atomic size and it is also a carbide-forming element. Both of these factors contribute to an improvement of creep properties of the alloy when tungsten is added. The amount of tungsten that is added is a balance between improving the creep properties, and limiting the high temperature resulting plastic deformation elongation involved by its presence There are diminishing returns in this improvement, on the one hand and the expense of adding tungsten, on the other hand. In some embodiments, the amount of tungsten is from 0.05 wt% to 0.15 wt%, and more preferably is from 0.05 wt% to 0.10 wt%. In certain embodiments, the amount of tungsten is preferably from 0.01 wt% to 0.05 wt%.

[0050] In certain alternative embodiments of the invention, the tungsten can be replaced by tantalum for the same purpose. In this circumstance, there would be no tungsten present in the alloy and the amount of tungsten would then be replaced by the same amount of tantalum. In these alternative embodiments, the amount of tantalum would therefore be from 0.01wt% to 0.25 wt%, with similar sub-ranges being preferred for tantalum as described above in relation to tungsten. However, it is preferable that tungsten is used instead of tantalum. In certain embodiments, both tungsten and tantalum could be used in amounts such that the total amount of both elements is from 0.01 wt% to 0.25 wt%.

YTTRIUM

[0051] The yttrium is present in an amount of from 0.01 wt.% to 0.25 wt.%, and preferably is present in an amount of from 0.01 wt.% to 0.05 wt.%. A particularly preferred amount is from 0.03 wt% to 0.05 wt%. Yttrium performs several roles in the alloys of the invention. Firstly, it serves to protect the addition of the aluminium in the melt, because the melt is formed in air melt rather than under a special protective atmosphere.

[0052] Yttrium is more reactive with oxygen than aluminium so it acts as a scavenger for oxygen.

[0053] In addition, yttrium, when present in small quantities modifies the primary carbide network shape making the resulting carbides thinner and more discontinuous, and consequently less brittle. Yttrium also has the benefit of improving the adherence of the surface oxide layer, acting as 'sink' for cavities.

[0054] It is not necessary to have a very large quantity of yttrium (another very expensive element) in the alloy to achieve these beneficial effects and an amount within the stated range is sufficient for this purpose. In some embodiments, the amount of yttrium is from 0.01 wt% to 0.03 wt%.

SILICON

[0055] Silicon is present in an amount up to 0.9 wt%. In some embodiments, silicon is present in an amount up to 0.6 wt%. In certain embodiments, the amount of silicon is from 0.6 wt% to 0.9 wt%. Silicon provides the function of a deoxidiser and is usually an essential component in an austenite stainless steel. Silicon may also contribute to increasing the stability of any surface oxide film. Silicon also provides some fluidity to the melt bath before the addition of the aluminium to the melt. On the other hand, if the content of silicon is too high the workability of the steel is reduced. A high Si content can also cause the formation of a detrimental phase known as the G phase which is composed of nickel, silicon and niobium ($Ni_{16}Nb_6Si_7$). Consequently, the amount of silicon must be carefully controlled. In some embodiments, the silicon is present in an amount of from 0.3 wt% to 0.6 wt%, and more preferably from 0.5 wt% to 0.6 wt%. In certain embodiments, the silicon may be absent or only a lower limit of silicon of 0.1 wt% is needed.

MANGANESE

[0056] Manganese is present in an amount of up to 0.9 wt%. Manganese can improve the workability of the alloy and it is also an effective de-oxidant and contributes to austenite formation in the steel. However, the high coefficient of diffusion of the manganese at high temperature means that it competes with the aluminium. Furthermore, the addition of too much manganese can result in a reduction in high-temperature strength and also toughness over an extended period of time. Consequently, the amount of manganese must be limited to 0.9 wt%. In some embodiments, the manganese is present in an amount from 0.4 wt% to 0.8 wt%, and more preferably from 0.4 wt% to 0.6 wt%. In certain embodiments, the manganese is present in an amount of from 0.7 wt% to 0.9 wt%. In certain embodiments, the manganese may be absent or only a lower limit of manganese of 0.1 wt% is needed.

NITROGEN

[0057] Nitrogen is inevitably present in the alloys of the invention. It is present in an amount of up to 0.10wt.%. Nitrogen may be found in the alloy because the alloy mix is prepared under an air atmosphere so it is often the case that nitrogen can diffuse into the liquid alloy during its production. However, it is not always possible to determine the amount of nitrogen in the alloy because the amount is insignificant and / or unmeasurable and in these cases the effective amount of nitrogen is almost zero. The absence of measurable nitrogen is not a detriment. Equally, in certain cases there is a measurable amount of nitrogen and in these cases the upper limit is 0.10 wt%.

[0058] Nitrogen forms austenite together with carbon and it contributes to high-temperature strength. Nitrogen allows the dilution, dispersion, and the homogenisation of the carbon. However, careful control of the amount of nitrogen is important because it slows the precipitation of primary chromium carbides when it is added in a suitable quantity. In effect, the nitrogen helps to control the 'behaviour' of the carbon so to control its several precipitations. The nitrogen participates in the precipitation of secondary niobium carbides, niobium carbido-nitrides, and niobium nitrides during ageing which are more stable than carbides at high temperature and therefore have better creep properties. However, if the quantity of nitrogen is too large then an excessive amount of nitrides are produced as chromium nitrides and/or aluminium nitrides which reduces the ductility and the toughness of the alloy over an extended period of time and prevent the 'nitrided' elements to fulfil their role in the alloy as they should. It is therefore essential to keep the amount of nitrogen present to a maximum of 0.10 wt%. There is however no practical lower limit to the measurable nitrogen in an alloy sample of the invention.

[0059] Alloys according to the present invention are produced in a conventional furnace and without the need for a special atmosphere. The first stage of preparing the alloy involves working out the relative proportions by weight of the various component minerals (which are the source of the various elements required in the final alloy) in order to achieve the desired amounts of the various elements which are required in the final alloy. The solid minerals are added to the hot furnace. Heating is continued in order to melt all of the mineral components together and ensure a thorough mixing of the minerals in the furnace so that the elements are properly distributed within the matrix.

[0060] In circumstances in which the addition of a particular essential element in the alloy composition of the invention also results in the addition of another essential element (because the other essential element is perhaps present as an impurity in the addition agent for the first essential element) then the overall composition must be carefully monitored to ensure that all of the essential components remain within the desired parameters. If necessary, this can be compensated for by adjusting the relative proportions of additional materials used for each of the essential components in the alloys of the invention. Sometimes elements are added in the form of preformed alloys, for example ferrotitanium might be used as a source of titanium and consequently the elemental calculations are adapted as necessary so that the required amount of the element (titanium in that particular example) is correctly added. The skilled person will be able to analyse and compensate as necessary for variations in the essential elemental components due to the presence of incidental impurities using known analytical techniques and by varying the amounts of the usual addition agents for each essential component.

[0061] A number of elements will be present in the alloy as inevitable impurities. Such incidental elements will not have any discernible technical benefit or adverse effect on the alloys of the present invention. In some cases, the presence of such elements, as the nitrogen can be tolerated in relatively large amounts provided that they do not affect the desired properties of the alloy. For example, although not specifically envisaged in the alloys of the present invention, it is conceivable that an element may arise as an incidental impurity as a consequence of its occurrence as an impurity in one of the deliberately added elemental components. This is acceptable provided that the presence of such an element does not have any deleterious effects on the alloy. In certain cases, deliberately added elemental components such as titanium may bring with them other incidental elements. These can be generally tolerated as incidental impurities at low levels. Where analysis reveals that such impurities are unacceptable, an alternative source of the desired elemental component (free of damaging impurities) is used.

[0062] The minerals and elements of the alloy composition are careful added in an appropriate sequence in order to obtain the desired content for the final composition. It is also important to protect the aluminium when added to the melt and avoid its oxidation because the melting is performed in air.

[0063] Once melting and mixing has been achieved, any slag is decanted from the furnace in order to remove impurities and clean the bath of liquid alloy in the furnace. A sample of the molten alloy is then removed from the furnace, allowed to cool and analysed by x-ray fluorescence in order to determine its elemental composition. An adjustment to the composition may or may not be required at this stage to accommodate for any elemental mass loss due to volatility. The composition is adjusted by the addition of further minerals as necessary, and optionally re-analysed to ensure that the desired composition has been achieved.

[0064] After the desired composition has been achieved, the temperature is further raised above the melting temperature to a tapping temperature in order to ensure easy pouring of the melt. At the same time, the mould is prepared for centrifugal casting.

[0065] The mould is a conventional centrifugal casting mould and this type of mould is well known to the skilled person. The process of preparing the mould involves washing the mould with water/steam to clean it and to remove any old mould wash or coating that might have been used in a previous casting process. The washed mould is then coated with an insulating/release agent which is required to prevent the alloy from sticking to the mould after casting. A typical insulating/release agent is silica or alumina.

[0066] A disc of ceramic is then added to the centrifugal casting mould in the manner known in the art in order to ensure that the mould is liquid tight and ready for casting. This prevents any alloy leakage during the casting process. The mould temperature is adjusted in preparation for the casting and may be in the range of 200° to 300° C. The mould is then rotated at high speed to obtain usually the range of 80g to 120g, with a rotation providing 100g being typical for a centrifugal casting speed.

[0067] A ladle is then brought to the furnace and a desired weight of molten alloy is tapped off for the purposes of casting including the relevant additions, such as titanium and yttrium, in order to reach the final desired quantity of aluminium and other reactive elements of the alloy composition. The ladle itself is preheated to a temperature in the region of 800° to 1000° C in order to minimise cooling of the alloy after pouring. Alloy is then transferred to the hot ladle. At this stage, a further analysis of the alloy may be performed.

[0068] The molten alloy in the ladle is then transferred to a pouring cup. The nose of the pouring cup has previously been adjusted to ensure that it mates with and properly fits the size of the input tube for the centrifugal casting mould. The level of molten alloy in the pouring cup is maintained in order to maintain adequate flow of alloy into the mould which is in effect fed by gravity. This provides a continuous flow of alloy into the mould until all of the weight of the alloy has been poured into the mould. The mould is rotated at high speed i.e. maintained at the centrifugal casting speed during the process and whilst the alloy is molten. The length of time the casting process takes depends ultimately on the desired thickness of the tube required and the skilled person is able to determine a suitable rotation time for a particular thickness of tube and weight of alloy. The mould is gradually slowed down as the alloy cools from its solidification point. Generally speaking, a "fast" solidification process is one in which the alloy is cast and then cools at a rate of more than about 100° C per minute and a "slow" solidification process is one in which the alloy is cast and then cools at a rate of about 50° C or greater per minute. The casting process is usually completed in less than about 10 minutes. The tube is extracted after the mould stops and the process may be repeated again.

[0069] The steel tubes of the present invention show excellent high-temperature strength and high creep resistance. The tubes also display exceptional corrosion resistance at elevated temperatures over an extended period of time. Consequently, these steels are particularly suited to use in chemical plant under demanding environments such as steam cracking. In addition, it is expected that steel tubes according to the invention may be used in a variety of other applications such as steam reformers and in nuclear applications in heat exchanges and the like, such as those found in pressurised water reactors.

[0070] The alloys of the invention were tested to demonstrate effective formation of alumina (aluminium oxide) on the surface in the hostile environment of a pack-carburisation test at 1100C over a period of 200hrs for an alloy containing 3.86 wt% aluminium. The alloy composition is shown in Table 1 below:

Table 1

	C	Ni	Cr	Nb	Si	Mn	W	Ti	Y	Al
wt%	0.25	43.3	29.6	0.81	0.56	0.54	0.05	0.11	0.01	3.86

[0071] The alloy was analysed by E.D.X (Energy Dispersive X-Ray). EDX cross section surface mapping identifies the oxide layer elements in the composition across its entire thickness and enables comparison with the alloy composition immediately below. Each of the elements in the alloy composition possess a characteristic X-ray line as Kα, and in the EDX map a greater quantity of a particular element in an area is indicated by increased brightness in the area.

[0072] Some of the key technical benefits of the invention can be seen from the following Figures in which:

Figure 1 shows an alloy according to the invention which has been subjected to EDX cross section surface mapping at the relatively low magnitude of 500X.

[0073] It can be observed from Figure 1 that the aluminium and oxygen appear in the alloy sample according to the invention as one very bright and continuous line. This indicates two things. Firstly, the aluminium and oxygen are present in a very high concentration, as alumina, at the exact same position where the surface oxide layer is observed by SEM photo (Scanning Electron Microscope). Secondly, there is a continuous layer of alumina at the surface of the material.

[0074] This analysis demonstrates that there is a dense, adherent, thin, continuous alumina (aluminium oxide) layer at the surface of the alloy even after pack-carburisation at 1100C over a period of 200hrs. It can also be seen that the alumina layer stays very stable and therefore does not get transformed in aluminium carbide, and acts as a protective layer i.e. a barrier against carburisation

[0075] Figure 2 shows EDX surface mapping at the higher magnification of 2000X for an alloy according to the invention having the composition shown in Table 1. In Figure 2, it can be seen that the aluminium and oxygen appear as the brightest components, and hence are present in very high concentration. In addition, it can be seen that these elements appear at the exact same position where the surface oxide layer is observed by SEM. A further important feature is the dark areas in the Figure which indicate the absence of elements such as nickel, iron and chromium. Figure 2 also illustrates the dense, adherent, thin, continuous alumina surface layer and indicates that it is pure, and free of highly catalytic elements as nickel and iron. The continuous surface layer and the absence of catalytic elements contribute to the anti-coking effect of the alloy when exposed to an external source of carbon. It can be seen from Figure 2 that the alumina layer is anti-coking, and does not bond or react catalytically with carbon during pack-carburisation at 1100C over a period of 200hrs.

[0076] Figure 3 shows is a High Magnification SEM Photo of the carburised surface of the alloy according to the invention having the composition of Table 1 (an alloy containing 3.8 wt.% Aluminium). The photograph clearly illustrates a continuous protective alumina layer at the surface. The thickness of the alumina layer was determined to be $4.28 \pm 1.21\ \mu m$ on the basis of 100 measurements.

[0077] It can therefore be seen that the alloys of the invention demonstrate superior properties in terms of the carburisation resistance and also exhibit resistance to oxidation on account of the alumina layer which can be formed in situ on the alloys in use.

[0078] Alloys of the present invention can be tested using a thermal oxidation cycle test. This test involves cycling the alloy through high and low temperatures over an extended time period in order to expose the alloy to oxidative stress. This test is frequently used for studying the oxidation characteristics of materials such as the superalloys / superalloys coating employed in gas turbines which are intended for high temperature use and / or use under extreme condition.

[0079] The test machine consists of a furnace brought to the test temperature and a sample handling apparatus which is able to introduce and remove the sample from the furnace very quickly in order to facilitate rapid heating and rapid cooling. The alloys of the present invention were tested at 1150° C. The higher the temperature, the faster growth of the oxide layer, so a thick oxide layer is likely to be formed.

[0080] The sample handling apparatus is a mechanism for bringing the test sample quickly in and out the furnace. The higher the furnace temperature, more extreme the thermal shock on the sample as it is introduced into and removed from the furnace. Repeated exposure of the sample under these conditions leads to the potential spallation of the oxide layer. The adhesion and thickness of the resulting oxide layer on the surface can then be investigated and used as a basis for establishing the performance of the alloys of the invention relative to those of the prior art.

[0081] The alloys of the invention were tested by repeating the heat-shock exposure through 50 cycles. Figure 4 of the drawings illustrates the temperature profile in the thermal oxidation test. The samples were pre-oxidised at 875° C over a period of 48 hours. Subsequently, the samples were exposed to 50 cycles in and out of the furnace and the temperature profile is shown in Figure 4. Each cycle consists of heating the sample under test from room temperature by introducing it into the furnace at 1150° C, keeping sample in the furnace for 45 minutes at that temperature in an atmosphere of air, and then removing the sample from the furnace and cooling it to room temperature over a period of 15 minutes. In the graph of Figure 4, the vertical axis represents both the temperature of the sample in degrees centigrade and also the air pressure in millibars. It can be seen from the graph that the air pressure in millibars is just slightly less than 1000 millibars (approximately 975 mbar). It can also be seen from the graph that the maximum temperature achieved in the heating cycles is 1150° C and that the minimum temperature, represented by the inverse peaks in the graph, is effectively room temperature. The horizontal axis in the graph indicates the time in hours throughout the test.

[0082] The repetitive nature of the test effectively exposes the sample to both mechanical fatigue and thermal fatigue so that the effects at the interface between bulk sample and its oxide surface can be investigated. The rate of growth of the oxide layer is measured as the sample is exposed to high temperature. The amount of stress and spalling of the oxide layer can therefore be viewed as the oxide layer develops.

[0083] The mass change of the sample is recorded before and after the test in order to assess the stability of the oxide layer. It is expected that the mass of any sample exposed to these harsh conditions will change because the test is very severe. However, a smaller variation in the mass before and after the test is indicative of a more stable and adherent oxide layer. This in turn is indicative of stability of the alloy over an extended period such as during long term service. The results achieved using alloys according to the invention are very impressive.

[0084] Figure 5 shows the compositions of three alloys according to the invention which were subjected to the thermal oxidation test.

[0085] Figure 6 shows photographs of the three samples after the Thermo-oxidation test and the variation of mass for each of the samples. It can be seen from Figure 6 that the variation of mass after test is negligible (all show a mass change of less than 1.15mg) and consequently that the alloys of the invention demonstrate excellent stability under these conditions. This also demonstrates that the alloys will be stable during an extended period in use.

[0086] Figure 7 illustrates the cross section of the surface of Sample C of Figure 5 after 50 thermo-oxidation cycles. This is investigated by X-ray spectroscopy using copper Kα radiation. It can be seen that there is a continuous oxide layer which is present across the majority of the sample. The oxide thickness is 3.61μm ± 0.61μm (based on 137 measurements). Figure 7 also highlights the scale of the aluminium and oxygen components of the alloy, as well as the scale of the nickel plating in the alloy.

[0087] The thermo-oxidation test results demonstrate that the alloys of the invention have a good resistance to oxidation under extreme conditions. These results also show that the alloys will have a long service lifetime.

Claims

1. An alloy comprising:

from 0.15 to 0.35 wt% carbon,
from 2.5 to 5.0 wt% aluminium,
from 40 to 45 wt% nickel,
from 25 to 35 wt% chromium,
from 0.50 to 1.50 wt% niobium and / or vanadium,
from 0.01 wt% to 0.25 wt% yttrium,
from 0.01 wt% to 0.25 wt% tungsten and / or tantalum,
from 0.01 wt% to 0.25 wt% in total of one or more of titanium and / or zirconium and / or hafnium,
up to 0.9 wt% manganese,
up to 0.9 wt% silicon, and
up to 0.10 wt% nitrogen,
with the balance of the composition being iron and incidental impurities,
optionally wherein up to 75 wt% by weight of the nickel is replaced with cobalt.

2. An alloy as claimed in claim 1, comprising:

from 0.15 to 0.35 wt% carbon,
from 2.5 to 5.0 wt% aluminium,
from 40 to 45 wt% nickel,
from 25 to 35 wt% chromium,
from 0.50 to 1.50 wt% niobium, and / or vanadium
from 0.01 wt% to 0.05 wt% yttrium,
from 0.05 wt% to 0.25 wt% of tungsten and / or tantalum,
from 0.04 wt% to 0.15 wt% in total of one or more of titanium and / or zirconium and / or hafnium,
an amount of up to 0.9 wt% manganese,
an amount of up to 0.6 wt% silicon, and
an amount of up to 0.10 wt % nitrogen,
with the balance of the composition being iron and incidental impurities optionally wherein up to 75 wt% by weight of the nickel is replaced with cobalt.

3. An alloy as claimed in claim 1 or 2, wherein carbon is present in an amount of from 0.20 wt% to 0.35 wt%.

4. An alloy as claimed in claim 1, 2 or 3, wherein aluminium is present in an amount of from 3.5 wt% to 4.5 wt%.

5. An alloy as claimed in claim 1, 2, 3 or 4, wherein nickel is present in an amount of from 42 wt% to 45 wt%.

6. An alloy as claimed in any preceding claim, wherein chromium is present in an amount of from 28 wt% to 30 wt%.

7. An alloy as claimed in any preceding claim, wherein niobium is present in an amount of from 0.80 wt% to 1.50 wt%.

8. An alloy as claimed in any preceding claim, wherein silicon is present in an amount of from 0.3 wt% to 0.6 wt%.

9. An alloy as claimed in any preceding claim, wherein manganese is present in an amount of from 0.4 wt% to 0.8 wt%.

10. An alloy as claimed in any preceding claim, wherein tungsten is present in an amount of from 0.05 wt% to 0.15 wt%.

11. An alloy as claimed in any preceding claim, wherein titanium is present in an amount of from 0.08 wt% to 0.15 wt%.

12. An alloy as claimed in any preceding claim, wherein yttrium is present in an amount of from 0.01 wt% to 0.03 wt%.

13. An alloy as claimed in any preceding claim, wherein nitrogen is present in an amount of from 0.03 wt% to 0.06 wt%.

14. An alloy as claimed in any preceding claim, wherein between 1 wt% and 75 wt% by weight of the nickel is replaced with cobalt, optionally wherein between 5 wt% and 15 wt% by weight of the nickel is replaced with cobalt.

15. A steel pipe made from an alloy according to any of claims 1 to 14.

Patentansprüche

1. Legierung, umfassend:

von 0,15 bis 0,35 Gew.-% Kohlenstoff,
von 2,5 bis 5,0 Gew.-% Aluminium,
von 40 bis 45 Gew.-% Nickel,
von 25 bis 35 Gew.-% Chrom,
von 0,50 bis 1,50 Gew.-% Niob und / oder Vanadium,
von 0,01 Gew.-% bis 0,25 Gew.-% Yttrium,
von 0,01 Gew.-% bis 0,25 Gew.-% Wolfram und / oder Tantal,
von 0,01 Gew.-% bis 0,25 Gew.-% insgesamt von einem oder mehreren von Titan und / oder Zirkonium und / oder Hafnium,
bis zu 0,9 Gew.-% Mangan,
bis zu 0,9 Gew.-% Silizium und
bis zu 0,10 Gew.-% Stickstoff,
wobei der Rest der Zusammensetzung aus Eisen und zufälligen Verunreinigungen besteht,
wobei optional bis zu 75 Gew.-% des Nickels durch Kobalt ersetzt sind.

2. Legierung nach Anspruch 1, umfassend:

von 0,15 bis 0,35 Gew.-% Kohlenstoff,
von 2,5 bis 5,0 Gew.-% Aluminium,
von 40 bis 45 Gew.-% Nickel,
von 25 bis 35 Gew.-% Chrom,
von 0,50 bis 1,50 Gew.-% Niob und / oder Vanadium
von 0,01 Gew.-% bis 0,05 Gew.-% Yttrium,
von 0,05 Gew.-% bis 0,25 Gew.-% Wolfram und / oder Tantal,
von 0,04 Gew.-% bis 0,15 Gew.-% insgesamt von einem oder mehreren von Titan und / oder Zirkonium und / oder Hafnium,
eine Menge von bis zu 0,9 Gew.-% Mangan,
eine Menge von bis zu 0,6 Gew.-% Silizium und
eine Menge bis zu 0,10 Gew.-% Stickstoff,
wobei der Rest der Zusammensetzung aus Eisen und zufälligen Verunreinigungen besteht optional wobei bis

zu 75 Gew.-% des Nickels durch Kobalt ersetzt sind.

3. Legierung nach Anspruch 1 oder 2, wobei Kohlenstoff in einer Menge von 0,20 Gew.-% bis 0,35 Gew.-% vorhanden ist.

4. Legierung nach Anspruch 1, 2 oder 3, wobei Aluminium in einer Menge von 3,5 Gew.-% bis 4,5 Gew.-% vorhanden ist.

5. Legierung nach Anspruch 1, 2, 3 oder 4, wobei Nickel in einer Menge von 42 Gew.-% bis 45 Gew.-% vorhanden ist.

6. Legierung nach einem vorhergehenden Anspruch, wobei Chrom in einer Menge von 28 Gew.-% bis 30 Gew.-% vorhanden ist.

7. Legierung nach einem vorhergehenden Anspruch, wobei Niob in einer Menge von 0,80 Gew.-% bis 1,50 Gew.-% vorhanden ist.

8. Legierung nach einem vorhergehenden Anspruch, wobei Silizium in einer Menge von 0,3 Gew.-% bis 0,6 Gew.-% vorhanden ist.

9. Legierung nach einem vorhergehenden Anspruch, wobei Mangan in einer Menge von 0,4 Gew.-% bis 0,8 Gew.-% vorhanden ist.

10. Legierung nach einem vorhergehenden Anspruch, wobei Wolfram in einer Menge von 0,05 Gew.-% bis 0,15 Gew.-% vorhanden ist.

11. Legierung nach einem vorhergehenden Anspruch, wobei Titan in einer Menge von 0,08 Gew.-% bis 0,15 Gew.-% vorhanden ist.

12. Legierung nach einem vorhergehenden Anspruch, wobei Yttrium in einer Menge von 0,01 Gew.-% bis 0,03 Gew.-% vorhanden ist.

13. Legierung nach einem vorhergehenden Anspruch, wobei Stickstoff in einer Menge von 0,03 Gew.-% bis 0,06 Gew.-% vorhanden ist.

14. Legierung nach einem vorhergehenden Anspruch, wobei zwischen 1 Gew.-% und 75 Gew.-% des Nickels durch Kobalt ersetzt sind, wobei optional zwischen 5 Gew.-% und 15 Gew.-% des Nickels durch Kobalt ersetzt sind.

15. Stahlrohr, hergestellt aus einer Legierung nach einem der Ansprüche 1 bis 14.

Revendications

1. Alliage comprenant :

   de 0,15 à 0,35 % en poids de carbone,
   de 2,5 à 5,0 % en poids d'aluminium,
   de 40 à 45 % en poids de nickel,
   de 25 à 35 % en poids de chrome,
   de 0,50 à 1,50 % en poids de niobium et/ou de vanadium,
   de 0,01 % en poids à 0,25 % en poids d'yttrium,
   de 0,01 % en poids à 0,25 % en poids de tungstène et/ou de tantale,
   de 0,01 % en poids à 0,25 % en poids au total d'un ou plusieurs éléments parmi le titane et/ou le zirconium et/ou le hafnium,
   jusqu'à 0,9 % en poids de manganèse,
   jusqu'à 0,9 % en poids de silicium, et
   jusqu'à 0,10 % en poids d'azote,
   le reste de la composition étant constitué de fer et d'impuretés accidentelles, éventuellement jusqu'à 75 % en poids du nickel étant remplacés par du cobalt.

2. Alliage selon la revendication 1 comprenant :

   de 0,15 à 0,35 % en poids de carbone,
   de 2,5 à 5,0 % en poids d'aluminium,
   de 40 à 45 % en poids de nickel,
   de 25 à 35 % en poids de chrome,
   de 0,50 à 1,50 % en poids de niobium et/ou de vanadium,
   de 0,01 % en poids à 0,05 % en poids d'yttrium,
   de 0,05 % en poids à 0,25 % en poids de tungstène et/ou de tantale,
   de 0,04 % en poids à 0,15 % en poids au total d'un ou plusieurs éléments parmi le titane et/ou le zirconium et/ou le hafnium,
   une quantité allant jusqu'à 0,9 % en poids de manganèse,
   une quantité allant jusqu'à 0,6 % en poids de silicium, et
   une quantité allant jusqu' à 0,10 % en poids d'azote,
   le reste de la composition étant constitué de fer et d'impuretés accidentelles,
   éventuellement, jusqu'à 75 % en poids du nickel étant remplacé par du cobalt.

3. Alliage selon la revendication 1 ou 2, ledit carbone étant présent en une quantité allant de 0,20 % en poids à 0,35 % en poids.

4. Alliage selon la revendication 1, 2 ou 3, ledit aluminium étant présent en une quantité allant de 3,5 % en poids à 4,5 % en poids.

5. Alliage selon la revendication 1, 2, 3 ou 4, ledit nickel étant présent en une quantité allant de 42 % en poids à 45 % en poids.

6. Alliage selon l'une quelconque des revendications précédentes, ledit chrome étant présent en une quantité allant de 28 % en poids à 30 % en poids.

7. Alliage selon l'une quelconque des revendications précédentes, ledit niobium étant présent en une quantité allant de 0,80 % en poids à 1,50 % en poids.

8. Alliage selon l'une quelconque des revendications précédentes, ledit silicium étant présent en une quantité allant de 0,3 % en poids à 0,6 % en poids.

9. Alliage selon l'une quelconque des revendications précédentes, ledit manganèse étant présent en une quantité allant de 0,4 % en poids à 0,8 % en poids.

10. Alliage selon l'une quelconque des revendications précédentes, ledit tungstène étant présent en une quantité allant de 0,05 % en poids à 0,15 % en poids.

11. Alliage selon l'une quelconque des revendications précédentes, ledit titane étant présent en une quantité allant de 0,08 % en poids à 0,15 % en poids.

12. Alliage selon l'une quelconque des revendications précédentes, ledit yttrium étant présent en une quantité allant de 0,01 % en poids à 0,03 % en poids.

13. Alliage selon l'une quelconque des revendications précédentes, ledit azote étant présent en une quantité allant de 0,03 % en poids à 0,06 % en poids.

14. Alliage selon l'une quelconque des revendications précédentes, entre 1 % en poids et 75 % en poids du nickel étant remplacé par du cobalt, éventuellement entre 5 % en poids et 15 % en poids du nickel étant remplacé par du cobalt.

15. Tube en acier constitué d'un alliage selon l'une quelconque des revendications 1 à 14.

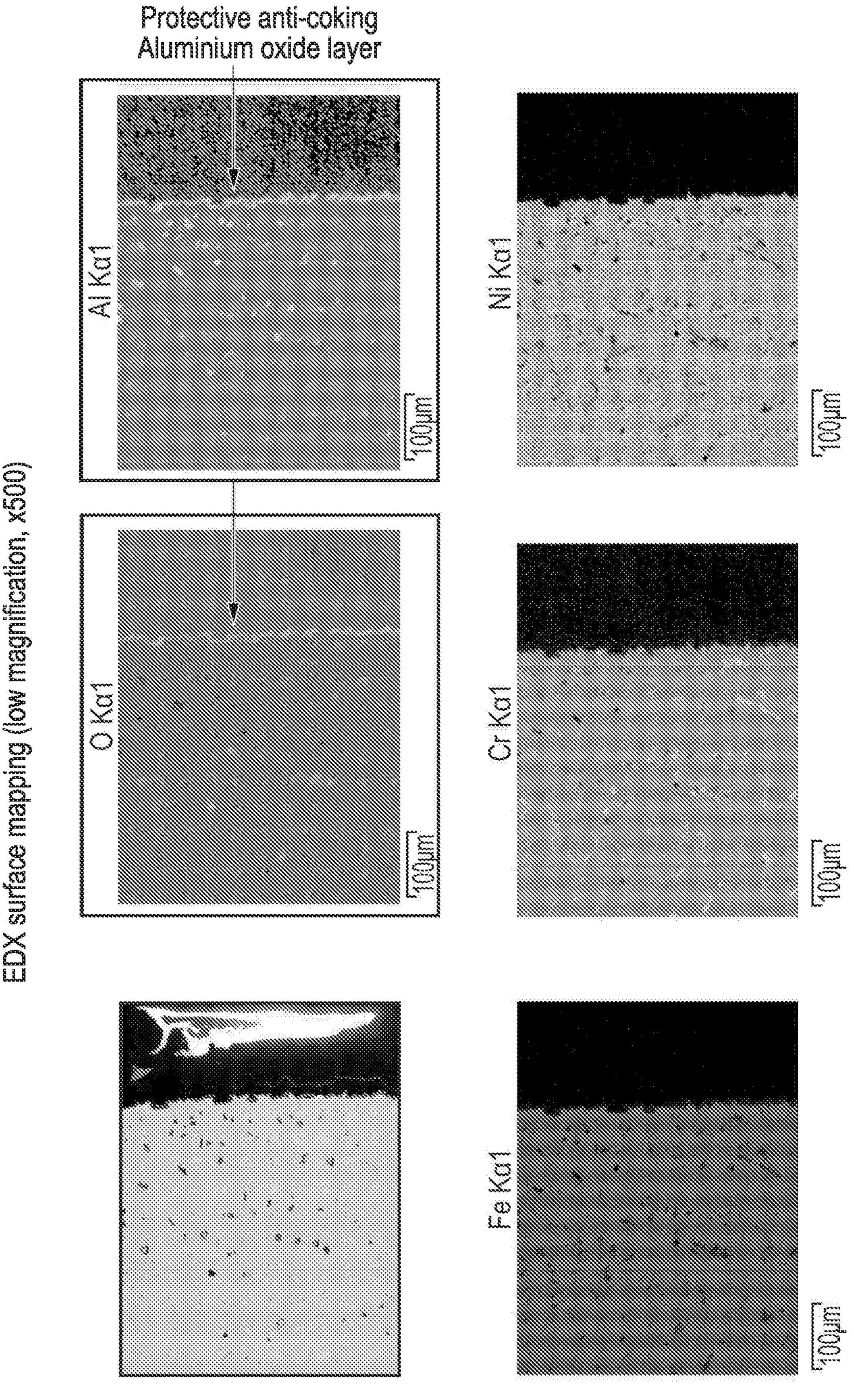

EDX surface mapping (low magnification, x500)
Protective anti-coking
Aluminium oxide layer
Al Kα1
O Kα1
Ni Kα1
Cr Kα1
Fe Kα1
100μm
100μm
100μm
100μm
100μm

FIG. 1

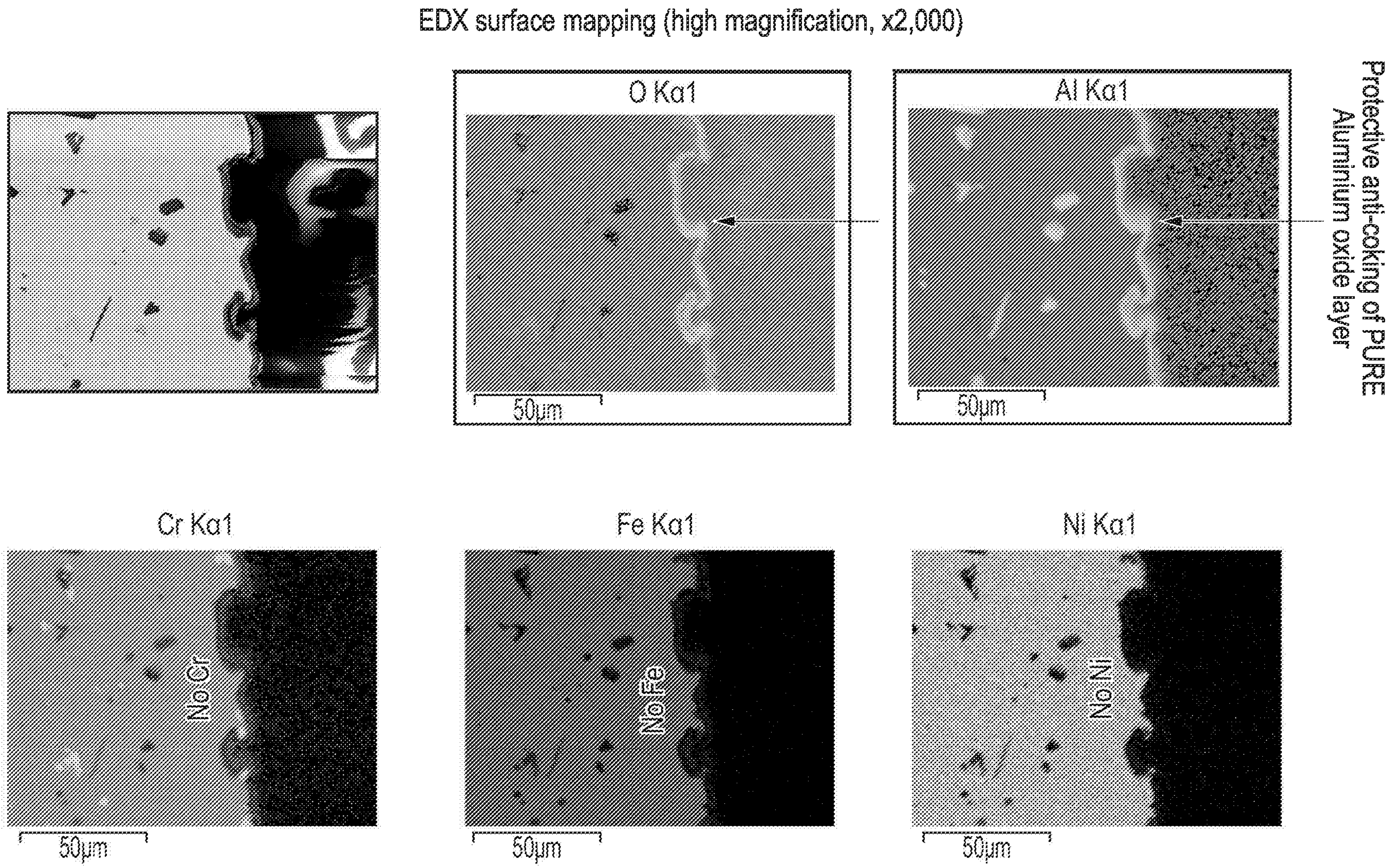
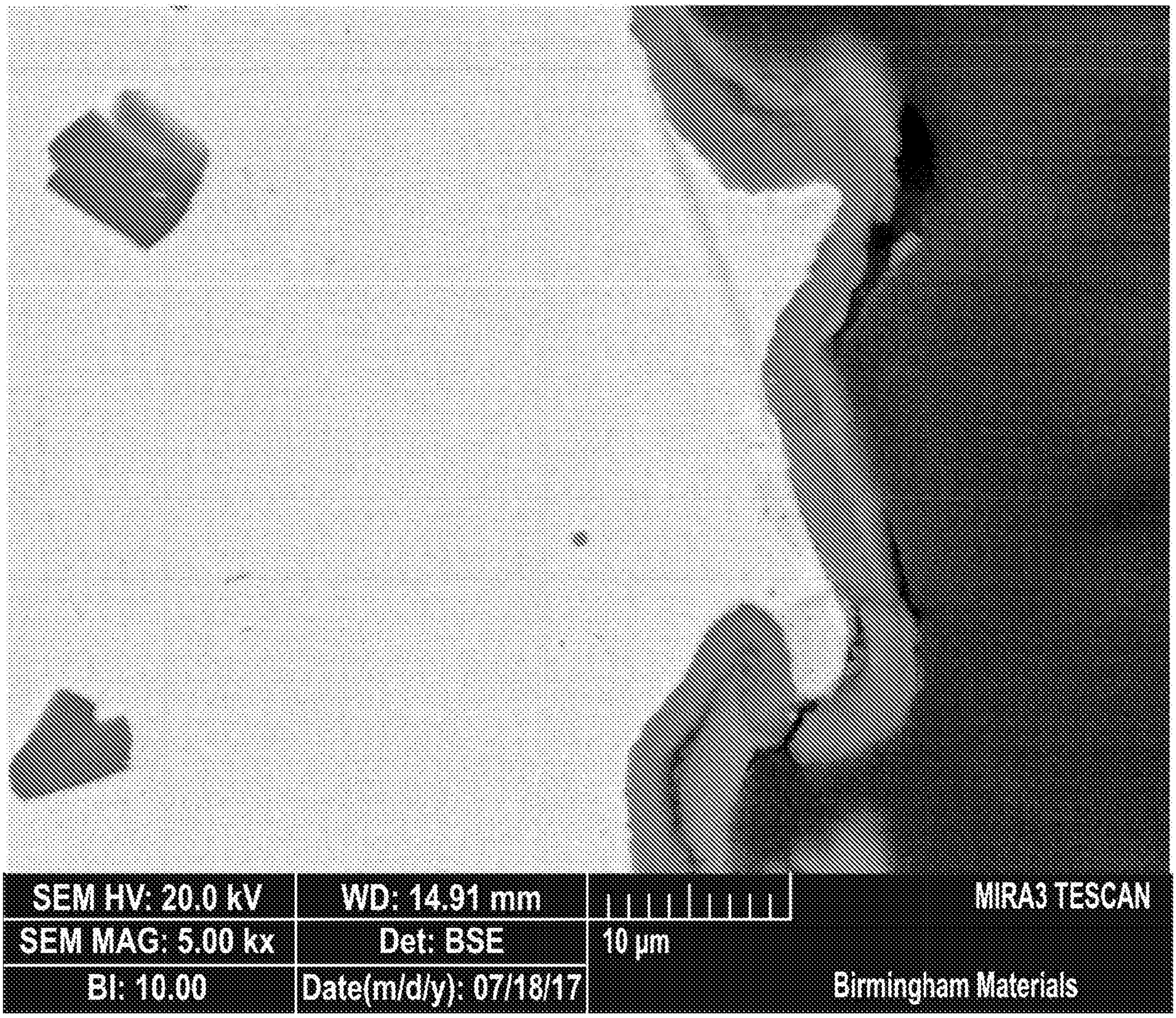

EDX surface mapping (high magnification, x2,000)
O Kα1
50µm
Al Kα1
50µm
Protective anti-coking of PURE Aluminium oxide layer
Cr Kα1
No Cr
50µm
Fe Kα1
No Fe
50µm
Ni Kα1
No Ni
50µm

FIG. 2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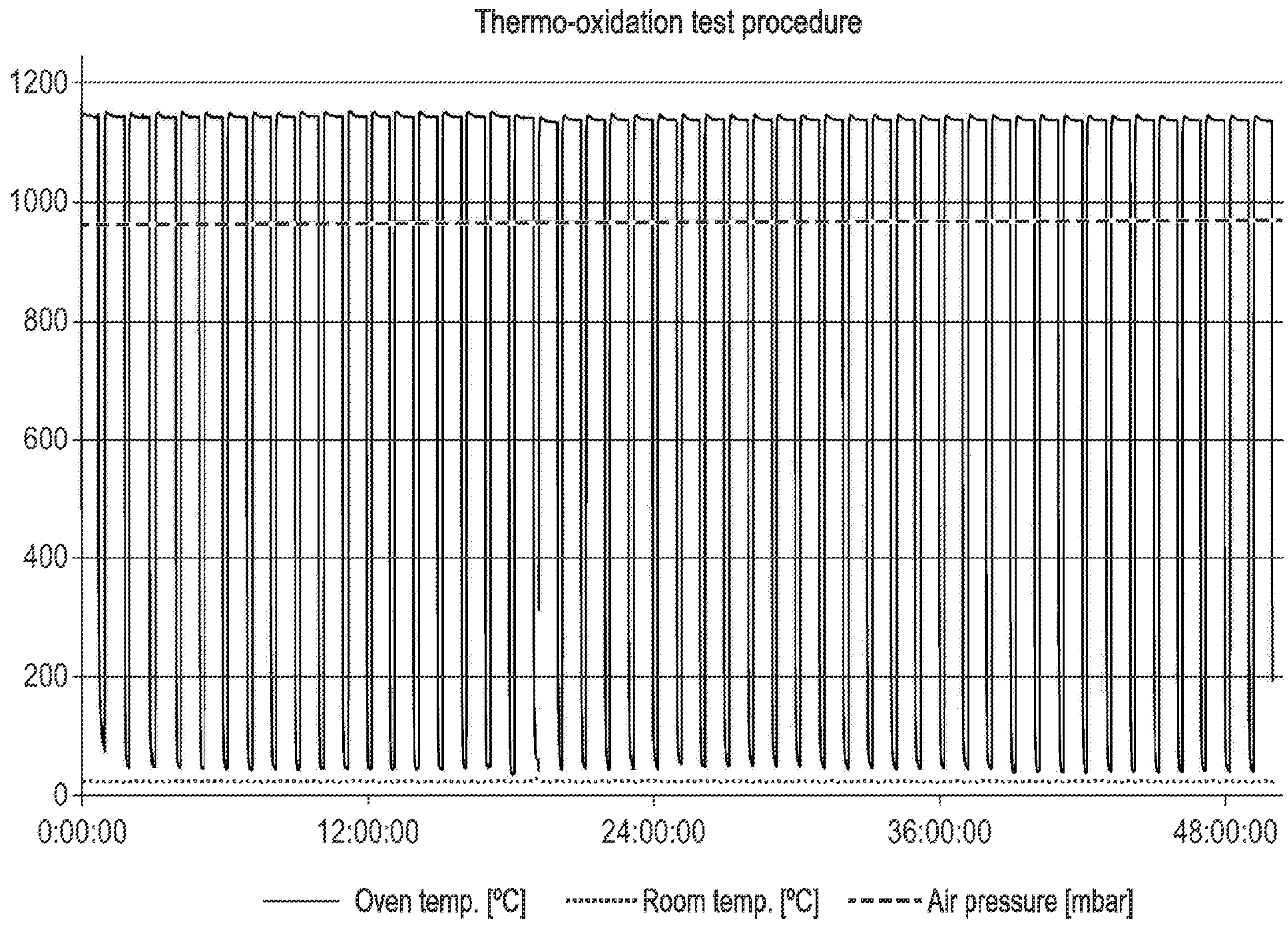
WD: 14.91 mm
MIRA3 TESCAN
SEM MAG: 5.00 kx
Det: BSE
10 µm
BI: 10.00
Date(m/d/y): 07/18/17
Birmingham Materials

FIG. 3


Thermo-oxidation test procedure
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1000
800
600
400
200
0
0:00:00
12:00:00
24:00:00
36:00:00
48:00:00
Oven temp. [ºC]
Room temp. [ºC]
Air pressure [mbar]

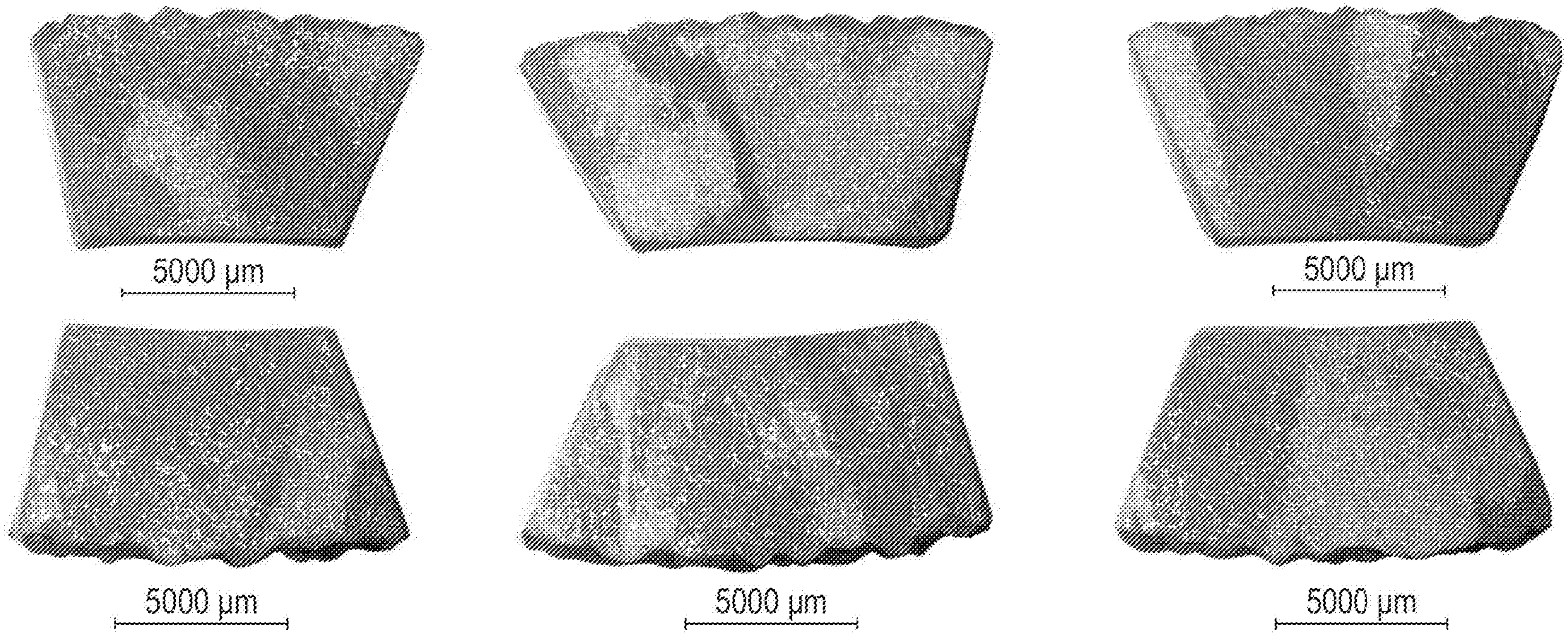
FIG. 4

Chemical composition of the 3 samples of the invention tested
using the thermo-oxidation test over 50 cycles

wt%	**C**	**Ni**	**Cr**	**Nb**	**Si**	**Mn**	**W**	**Ti**	**Y**	**Al**
A	0.27	42.7	28.3	0.85	0.61	0.75	0.04	0.12	0.01	4.00
B	0.28	43.2	30.1	0.95	0.75	0.87	0.05	0.10	0.01	3.27
C	0.25	42.2	26.2	1.05	0.62	0.76	0.04	0.13	0.01	4.53

FIG. 5

Photographs of samples after the thermo-oxidation test and variation of mass (Δm)



Sample A
(front/back)
$\Delta m = -0,15$ mg

Sample B
(front/back)
$\Delta m = -0,04$ mg

Sample C
(front/back)
$\Delta m = -1,14$ mg

FIG. 6

Sample C cross-section of the surface after 50 thermo-oxidation cycles

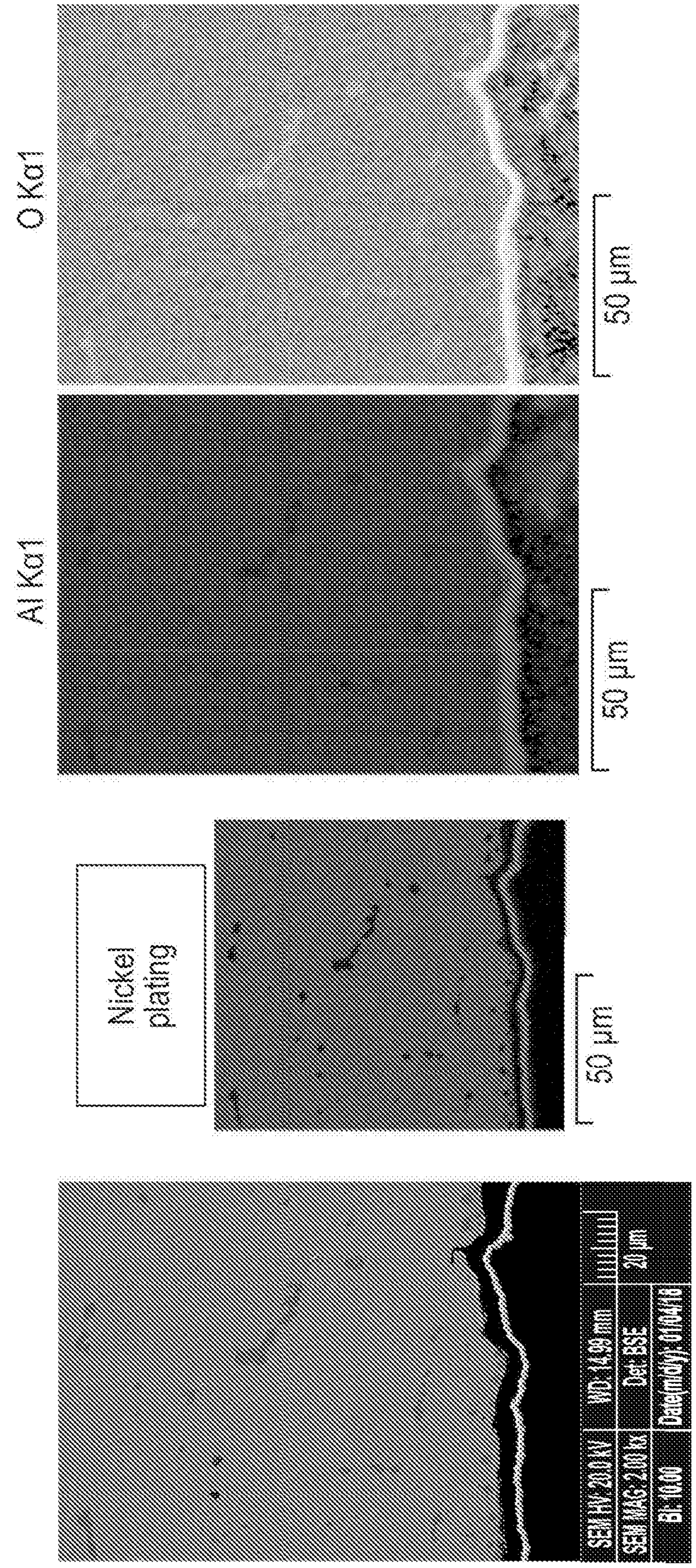


FIG. 7

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 64031931 B **[0005]**
- WO 2012121389 A **[0006]**
- WO 200022068 A **[0007]**
- US 2002192494 A **[0008]**
- US 2001001399 A **[0009]**