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METHODS OF FORMING SUPERFICIAL DIFFUSION ALLOYS ON METAL PIECES AND ESPECIALLY REFRACTORY METAL PIECES

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Fig. 1.

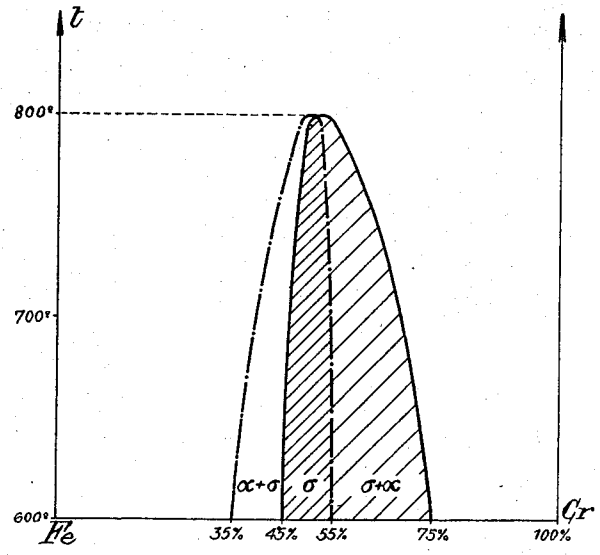
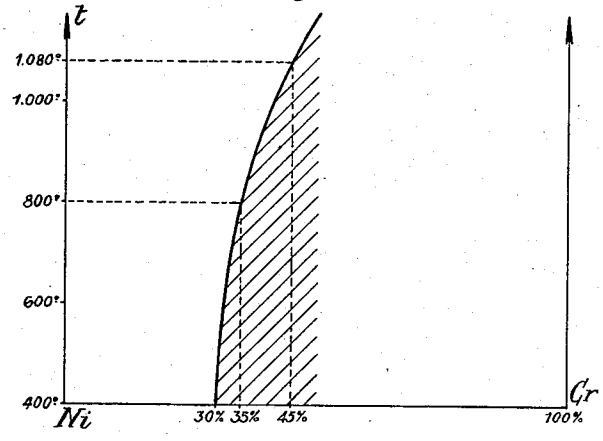


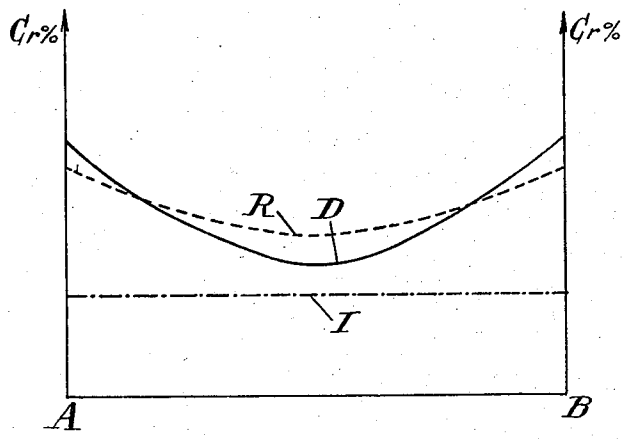
Fig. 2.



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Fig. 3.



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METHODS OF FORMING SUPERFICIAL DIFFUSION ALLOYS ON METAL PIECES AND ESPECIALLY REFRACTORY METAL PIECES

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14 Claims. (Cl. 117—50)

It is known to protect metal pieces and articles by superficially diffusing chromium (possibly with other addition metals) therein. In particular said pieces may be subjected, in a suitable container, to the chromizing action of "active" vapors of at least one chromium halide (chromium fluoride forming at least a portion of said vapors) evolved from a "cementation mixture" located out of contact with the pieces and which contains, either in the solid or in the liquid state, said halide or at least the elements for forming it in said container. The temperature of treatment ranges advantageously from 1050 to 1150° C. (the boiling point of CrF_2 is 1300° C.) and must anyway be lower than the boiling point of chromium fluoride. The treatment container may include a regeneration reserve of chromium, i. e. a mass of chromium for regenerating the chromium fluoride active vapors, which mass may be in contact with the pieces of treatment, in so-called semi-contact methods. The treatment container may also contain a diluting body added to the regeneration chromium mass. Such a treatment causes the formation, in the superficial layers of the treated pieces, of a diffusion alloy of chromium with the alloy of which said pieces are made.

The object of the present invention is to improve the resistance to corrosion and fatigue of refractory alloys, that is to say alloys having a good toughness at high temperatures, such alloys being superficially enriched with chromium (and possibly other addition metals) and being therefore designated by the term "chromized" refractory alloys.

In the case of pieces made of alloys consisting chiefly of iron and/or nickel, containing at least one other metal capable of giving refractory properties to the alloy (such for instance as chromium, molybdenum, cobalt, aluminium, titanium, manganese) and treated as above stated to enrich them with chromium, some of the chromium added by chromizing forms a solid solution with iron or nickel (or both) at high temperatures. When the temperature decreases subsequently, the chromium tends to precipitate in the form of compounds which produce on the surface of the piece hard but brittle areas which may scale off under the effect of temperature variations.

To eliminate this drawback, according to the present invention, the pieces are subjected, after the superficial chromizing operation, to a heating treatment in an inactive (i. e. non chromizing) atmosphere, consisting for instance of hydrogen or cracked ammonia so as to cause chromium from the external alloy layers to rediffuse into the mass of the pieces, whereby the percentage of chromium in said external layers is reduced sufficiently to prevent the formation of the above mentioned undesirable precipitates.

According to still another feature of the present invention, this treatment including a superficial chromizing (possibly with simultaneous diffusion of Si or Al) followed by a rediffusion by heating in an inactive atmosphere may be used to obtain thin pieces containing

throughout their mass a high percentage of chromium. This particular method is interesting to obtain by a shaping operation such as a mechanical deforming treatment (such as extruding, stamping, forging, etc.) or a sintering treatment a piece of an alloy which, if containing so high a percentage of chromium (and possibly of Si or Al), could not undergo such a shaping operation (mechanical treatment or sintering). The present invention makes it possible first to perform this treatment on an alloy containing a sufficiently low percentage of chromium (and possibly Si or Al), then by the above mentioned successive chromizing and rediffusion treatment to increase the chromium percentage throughout the piece, owing to the thinness thereof.

In the case of pieces made of alloys consisting chiefly of nickel and chromium and containing at least one auxiliary metal component, such as titanium and/or aluminum forming in the mass of the peices precipitations which achieve a structural hardening thereof, these precipitates which form particularly along the joints between metallic grains, and which do not contain chromium, form, in the superficial layers of a piece which contains chromium, even if said layers have been enriched in chromium, paths through which corrosion can propagate, said paths being on the other hand occupied by chromium compounds having no protective value (such as chromium carbide) which have got their chromium component at the expense of the adjoining areas, thus lowering the resistance of said areas to corrosion.

In order to eliminate this drawback, according to another feature of the present invention, these auxiliary metal components are, before the superficial chromizing operation, eliminated from the superficial layers of the pieces by subjecting said pieces to a controlled oxidizing which causes said auxiliary metal components to diffuse toward the surface of the pieces and by removing the external layer of oxides thus formed, for instance by electro-thermal sodium scouring.

When a piece made of a refractory alloy to be superficially chromized contains carbon, either free or in combination, if no precautions are taken this carbon, during the chromizing operation, tends to diffuse toward the surface of the piece where it combines with the diffused chromium so as to form chromium carbide which precipitates in the metallic grain joints, at the detriment of the chromium serving to protect the surface of the piece.

In order to prevent this, according to still another feature of the present invention, there is introduced, during the chromium diffusing operation, together with chromium at least one metal having a higher affinity than chromium with carbon (for instance zirconium, titanium, molybdenum, wolfram, manganese, vanadium), whereby combinations of this metal with carbon precipitate in the grains (instead of chromium carbide precipitating in the joints between grains).

The same result, to wit, to avoid the formation of undesirable chromium carbide, may be obtained, according to the present invention, by introducing into the piece, during the chromium diffusing operation, together with chromium, a suitable amount of silicon which forces back carbon toward the inside of the piece.

Preferred embodiments of the present invention will be hereinafter described with reference to the accompanying drawings in which Figs. 1, 2 and 3 are explanatory diagrams.

As above explained, the chromizing of metal pieces by superficial diffusion of alloys into the substance forming said pieces improves the resistance thereof to dry corrosion, especially when said pieces are intended to work at high temperature in a sulfurous and reducing atmosphere, which is the case in particular of some gas turbine elements made of alloys consisting chiefly of

nickel and/or iron such as the chromium and nickel alloys known under the name of "Nimonic."

It is interesting to know that the protective action of chromium in such conditions seems to be due to the formation of chromium sulfide the melting point of which is very high (about 1550° C.), whereas in the absence of a superficial layer rich in chromium, nickel sulfide would form the melting point of which is much lower (averaging 750° C.), whereby internal corrosion of the piece along the joints between the metallic grains would take place.

An increase in the percentage of chromium tends to enlarge the field inside and a good resistance of the alloy is obtained. For instance it was found that for pieces to be used in combustion gases the necessary percentage of chromium increases when the temperature of said gases increases. Thus, it may be admitted that, in order to have a satisfactory resistance at 850° C., the chromium percentage should be higher than 15%, at 900° C. higher than 20%, at 1000° C. higher than 30%.

However, as above stated, the superficial diffusion of chromium in proportions corresponding to the maximum percentage in a solid solution of chromium and iron or chromium and nickel at the temperature where chromizing takes place involves disadvantages. In particular, when the temperature is reduced below chromizing temperature, the chromium which had formed a solid solution in iron and/or nickel undergoes a partial precipitation which is accompanied by the formation of compounds which form on the surface of the piece hard but brittle zones which are liable to scale off and have a lower fatigue limit.

In order to obviate this drawback, according to my invention, the pieces, after the chromizing treatment proper, are subjected to a heating treatment in a reducing inactive atmosphere (i. e. a nonchromizing atmosphere) constituted for instance by hydrogen or cracked ammonia. In some cases, however, this atmosphere may contain a small amount of a fluoride compound (i. e. an amount insufficient to cause chromizing) if it is desired to maintain the bright surface state of the pieces. This complementary treatment may constitute a separate operation or it may be performed immediately after the chromizing operation, after the active (fluoride) vapors have been eliminated. The pieces may be strongly heated in order to activate the diffusion of chromium into the mass thereof. However this treatment should preferably be performed at a temperature not higher than 1300° C.

This complementary thermal treatment is effected at a temperature and for a time such that the superficial layer of the treated pieces finally contains a percentage of chromium (lower than that existing at the end of the chromizing treatment proper) corresponding to that which may be maintained without any inconvenience at the temperature of utilization of the pieces (or at ordinary temperature) and however higher than the percentage which achieves a satisfactory resistance to corrosion in the conditions of utilization.

This complementary heating treatment has for its effect to increase the thickness of the chromized layer by making the innermost layers richer in chromium at the expense of the external layers which initially contain the maximum percentage of chromium. Therefore in the course of this complementary treatment, what can be considered as an inward rediffusion of chromium takes place, and the percentage of chromium in the external layers is reduced so as to eliminate the risks of precipitates forming on the surface of the pieces hard but brittle zones. The same method is applicable if the superficial layers contain other addition metals such as Si and Al.

Figs. 1 and 2 illustrate the results thus obtained. These figures show solubility diagrams corresponding to an iron chromium alloy for Fig. 1 and a nickel chromium alloy for Fig. 2, the dangerous areas being cross-hatched.

These diagrams show that, in order to avoid the formation of brittle superficial areas, it suffices in the case of iron chromium superficial alloys, to perform rediffusion of chromium into the mass until the percentage of chromium in the superficial layer is lower than 45% approximately (the sigma phase incorporated in an alpha material is less dangerous). In the case of superficial alloys of nickel and chromium, the thermal treatment or heating is conducted in such manner as to obtain, in the superficial layer, a chromium percentage averaging 30–35% (according to the temperature at which the pieces are to be used).

It should be noted that the use of a piece in an oxidizing atmosphere will bring about a slight reduction of the chromium percentage in the superficial layers of this piece, due to the formation of Cr_2O_3. This slight percentage reduction may be taken into account when determining the percentage to be obtained at the end of the rediffusion operation.

Some examples of application of this feature will now be given.

A first application is concerned with a gas turbine element of special steel containing 18% of chromium and 8% of nickel. Chromizing with a chromium fluoride cementation mixture in approximately gas-tight boxes heated in a hydrogen atmosphere, for four hours at a temperature of 1100° C., makes it possible to obtain in the external superficial layer an amount of chromium averaging 65%. A rediffusion treatment as above described (i. e. a heating in a nonchromizing atmosphere) during two hours, at a temperature of 1125° C., advantageously followed by quenching in water at a temperature of 900° C. for instance, prevents the formation on the surface of the pieces of a sigma phase which is particularly dangerous because of its brittleness. The advantage thus obtained was still effective after the piece had been used for several hundreds of hours at a temperature of 650° C.

A second application of the invention relates to sheets of Nimonic 75 having, after a chromizing treatment of three hours at 1080° C. with a chromium fluoride cementation mixture, a superficial richness in chromium of 55.60%. A rediffusion treatment of three hours at 1080° C., or a similar treatment for one hour at 1125° C., makes it possible to obtain, for such chromized Nimonic sheets, external layers which are much more flexible and more resistant to thermal shocks.

A chromizing treatment applied to such Nimonic 75 pieces with a cementation mixture containing 50% of chromium fluoride and 50% of chromium chloride will give, after three hours at 1080° C., superficial layers containing from 40 to 50 percent of chromium. A rediffusion operation of one hour at 1100° C. makes it possible to lower this superficial percentage to 30–35%.

Gas turbine blades made of Nimonic 80 have also been treated in the same conditions and have shown an increase resistance both to fatigue and to corrosion.

Another particularly interesting application concerns the treatment of metal wires intended to be used as electric resistances (wires made of iron, nickel or alloys such as ferro-nickel, ferro-aluminium, ferro-nickel-aluminium, ferro-chromium, nickel-chromium, etc.). For instance, a wire of 2 mm. diameter made of an alloy containing 98% of iron and 2% of aluminium was chromized for two hours at 1100° C., after which chromium rediffusion was performed by heating for four hours at 1100° C. in a non chromizing atmosphere. After treatment, the wire was flexible and had a high resistance to dry corrosion at 1000° C. for several hundreds of hours.

Excellent results were also obtained with an analogous treatment with a wire consisting of an alloy of iron (85%), chromium (13%) and aluminium (2%), this wire after treatment having a good resistance at temperatures averaging 1125° C.

It is pointed out that, in the case of wires intended to be used as electrical resistors, it would be possible to dispense with the rediffusion heating treatment on account of the fact that this rediffusion is to take place when the wire is used as a resistor. As a matter of fact, when the wire is being fitted (generally by winding) on the utilization apparatus, the presence of a brittle portion on a surface would produce a superficial scaling off which would impair the life of the resistor once in service.

In order to proceed to the rediffusion treatment as above mentioned, the active vapors, that is to say the chromium halide (fluoride) vapors, possibly with other metal halide vapors, may be condensed in a cooled zone of the treatment container, after which the rediffusion heating treatment can take place. But it may happen that slight amounts of chromium halide in the solid or liquid state remain in this portion of the container and thus exert a chromizing action which is then no longer desired.

In order to avoid this drawback, according to the present invention, the halide condensation step is effected only after a quick heating at high temperature of the whole of the treated pieces and possibly the regeneration chromium mass so that, when condensation is performed, the whole of the halide (fluoride) is in the form of vapor and is therefore eliminated by this condensation.

This feature is particularly useful in the case of rediffusion since this operation is to be carried out without a supplementary addition of metal. In this case, of course, it is quite necessary to eliminate all the active vapors as may exist and to keep the condensation effect in the cooled portion of the treatment container while rediffusion is taking place. The above-mentioned quick heating can then be continuous during the rediffusion operation, and this heating, if maintained, accelerates this operation.

When the duration of the rediffusion operation and the temperature to be brought into play require at the end of this treatment a quenching of the pieces in an oxidizing liquid, in order to regenerate the fineness of the metallic grains, it may be desired to restore the superficial brightness of the pieces.

According to the present invention, the pieces are then subjected for a relatively short time, for instance some minutes, to a heating in an atmosphere of chromium halide vapors at a temperature, for instance of 950° C., higher than that sufficient to obtain a total reduction of the layer of oxide due to quenching, but lower than that which would produce a further superficial diffusion of addition metal since it has been admitted that the rediffusion operation reduced the superficial percentage to the desired value.

The last mentioned condition is important in order to prevent the formation of brittle superficial layers on the piece while keeping a correct structural state in the mass and a satisfactory surface appearance.

Of course, rediffusion immediately after chromizing may be obtained without having to produce condensation of the active vapors, if the amount of cementation mixture initially placed in the chromizing container is measured so that it is wholly consumed at the end of the chromizing operation.

As above stated, the rediffusion operation must be carried out in a nonchromizing atmosphere, for instance of hydrogen or cracked ammonia. But it should also be pointed out that, outside of exceptional cases (superficial hardening), this atmosphere must not contain any carburetted compound or any compound capable of giving off nascent nitrogen during the treatment.

The treatment of metal pieces which includes a superficial chromizing followed by rediffusion by heating of the pieces in an inactive atmosphere (one which does not contain chromizing vapors) may be used in order to obtain thin pieces of an alloy containing a high percentage of chromium distributed in a substantially uniform fashion throughout their mass.

It is known that alloys containing an amount of chromium equal to or higher than approximately 25% cannot undergo mechanical deformation treatments, such as extruding, stamping, forging, etc. Pieces made of alloys of such compositions can be obtained only by casting or sintering. And even these last mentioned operations may become much more difficult as a result of the presence of high percentages of chromium. The same difficulties exist for pieces intended to contain high percentages of Si and Al together with Cr.

According to the present invention, such pieces can be obtained in the following fashion, provided that these pieces are thin or have thin walls. It will be supposed that a piece containing a high percentage of chromium is to be shaped by mechanical deformation.

A blank made of a metal or alloy in which the percentage of chromium is lower than 25% is first formed. As a matter of fact, this percentage may be zero and in this case the blank is made of the metal with which chromium is to be added to form the desired alloy.

This blank is first subjected to the mechanical deformation treatment as above referred to, that is to say to stamping, forging, extruding or similar operation. This is possible because the amount of chromium in the blank is much lower than that which would prevent the possibility of this treatment.

After this operation, the piece is chromized on both of its faces, preferably by action of a fluoride vapor thereon, so as to form a chrominum superficial alloy on both of the faces of said piece. Then the chromizing atmosphere is withdrawn and the piece is heated so as to obtain a rediffusion as above mentioned, whereby the excess of chromium present in the external layers is diffused into the mass of the piece. In view of the fact that this piece is thin, the amount of chromium diffused toward the inside achieves a substantially uniform percentage of chromium throughout the whole mass.

It will be supposed for instance that the thickness of the piece ranges from 1 to 2 mm. and that said piece is to be made of a refractory alloy consisting chiefly of iron and nickel. It is desired to obtain a piece containing a percentage of nickel ranging from 25 to 30%.

On the diagram illustrated by Fig. 3, A and B represent the thickness of the piece and the chromium percentages are plotted in ordinates. In the initial state, that is to say in the blank formed initially, the percentage of chromium is represented by line I. After the chromizing operation, the chromium percentages are represented by D in solid lines. After the rediffusion operation, the chromium percentages are represented by line R in dotted lines.

Preferably, the initial alloy further contains at least one element such as tungsten, molybdenum, vanadium, capable of improving the mechanical characteristics of the piece, in particular in the hot state. Such auxiliary elements further have the advantage of accelerating and improving the diffusion of chromium, both during the chromizing operation and during the rediffusion operation in particular by opposing the diffusion of carbon toward the superficial layers.

The method which is being described makes it possible to achieve a quick addition of chromium, even into alloys which already contain a substantial proportion thereof in their mass, this initial proportion of chromium reducing the penetration of additional chromium from the superficial layers but giving at the start a uniform percentage in the mass of the piece.

For instance, it has been possible to obtain thin pieces (thickness of about 1 mm.) containing a high percentage of chromium from an alloy containing initially 18% of chromium, 10% of nickel, 4% of tungsten, 1% of titanium, the remainder being iron.

After the chromizing operation, performed in approximately gas-tight boxes heated in a hydrogen atmosphere,

which took place for fifteen hours at a temperature of 1120° C. with a cementation mixture supplying the chromium fluoride, the amount of chromium was 38% superficially and 20% inside the mass of the alloy.

After the rediffusion operation which also lasted for fifteen hours at a temperature of 1120° C., the percentage in the vicinity of the surface was reduced to 31% and the percentage inside the mass reached 24%.

With the same alloy and in the same apparatus conditions, with a cementation mixture consisting of chromium fluoride and nickel chloride (75% of CrF_2 and 25% of $NiCl_2$), the pieces being surrounded by particles of regeneration chromium, there was obtained, after a diffusion treatment of four hours at 1175° C. followed by a rediffusion in a non-chromizing atmosphere for four hours at 1250° C., percentage values of 39% in superficial layers and 19% in the mass, after the diffusion operation and of 29% in superficial layers and 22% in the mass, after the rediffusion operation.

With a similar alloy, but with a chromium percentage of 5% (5% of chromium, 10% of Ni, 4% of W, 1% of Ti, the remainder consisting of iron), with the same apparatus and with a cementation mixture containing 50% of $CrCl_2$ and 50% of $NiCl_2$, the pieces being surrounded by particles of regeneration chromium, the diffusion operation leasting 12 hours at 1150° C., there is obtained directly, i. e. without rediffusion, chromium percentages ranging from 30% superficially to 20% in the mass.

If this percentage range is acceptable, rediffusion may therefore be dispensed with. As a matter of fact, in this case, rediffusion is chiefly intended to increase the chromium percentage in subjacent layers because, when chromizing is carried out with cementation mixtures constituted only by chlorides, the superficial layers cannot contain percentages leading to the formation of brittle layers.

It is pointed out that, whereas, up to the present time, mention has been made only of chromizing, i. e. the diffusion of chromium into the pieces to be protected, all the methods above described might also apply to aluminium and silicon, and in particular to the mixed diffusion of chromium and at least one of said two other methods (to wit, aluminium and silicon).

Soft steel heat exchanger plates 2 mm. thick were subjected to a diffusion treatment of four hours at 1075° C., with a chromium fluoride cementation mixture containing some aluminium placed out of contact with said plates. A reserve of regeneration metal contained chromium and aluminium, with alumina as diluting element. The diffusion layers thus obtained contained superficially 30% of chromium and 30% of aluminum. The plates contained chromium to a depth of 0.7 mm. on every side and 5% of aluminum in the central portion. After rediffusion for eight hours at 1120° C., the percentage of Cr and Al became uniform throughout the whole of the piece and after drilling of the pieces it was found that their resistance to dry oxidizing was excellent for temperatures up to 1000° C. for several hundreds of hours.

Steel test pieces 1.5 mm. thick were subjected to a diffusion treatment for 5 hours at 1050° C. with a chromium fluoride cementation mixture containing some silicon, placed out of contact with these pieces, with a regeneration reserve of chromium. The diffusion layers obtained contained superficially 28% of Cr and 10% of Si and were very brittle. After rediffusion for six hours at 1100° C., it was found that, after drilling, the pieces could be used for mechanical purposes and resisted the attack of acids, and in particular nitric acid.

For instance, the method according to the present invention was applied to a mixed diffusion of chromium and aluminium and rediffusion into the pieces (so as to form thermo-couple sleeves). Initially, the pieces were made of a mere iron tube with a welded bottom, and the pieces finally obtained were capable of withstanding a temperature of 1050° C. for several hundreds of hours.

In a general fashion, the last mentioned method makes it possible to obtain pieces having good mechanical characteristics in the hot state (and in particular a high superficial hardness) and a high resistance to corrosion at high temperature against combustion gases even containing sulfur.

Such pieces may have a thickness as high as 2 mm. when only chromium is added by diffusion and 3 mm. when chromium and aluminum or chromium and silicon are added by diffusion.

It is very advantageous thus to obtain through a simple method, from relatively cheap alloys which can be shaped without difficulty, thin wall pieces having throughout their mass a high percentage of protective metals such as chromium or chromium and silicon, or chromium and aluminum. A mere superficial protection by means of known treatments can be applied only if the piece is treated after its having been machined. On the contrary, pieces enriched with protective metals throughout their mass can be finished after the diffusion and rediffusion operations have been performed and, for instance, can be drilled without risks of local corrosion taking place when said pieces are in service. To obtain this result the protective metal percentage must be higher than 13% in the mass to achieve satisfactory resistance to nitric acid or salt water and higher than 15–30% to achieve satisfactory resistance to combustion gases (according to their temperature, ranging from 850 to 1000° C.).

Furthermore, uniformity of the composition makes the physical properties (such as the coefficient of expansion) uniform throughout the mass which is advantageous for pieces to be used at high temperatures.

It should be pointed out that the presence of carbon in the pieces in treatment is undesirable because this carbon is fixed by the additional metals such as vanadium, titanium, molybdenum and manganese, to give carbides which are more stable than chromium carbide.

In the case of pieces made of alloys consisting chiefly of nickel and chromium and containing at least one auxiliary metal component such as titanium and/or aluminum forming in the mass of the pieces precipitations which achieve a structural hardening thereof, these precipitates, which form particularly along the joints between metallic grains and which do not contain chromium, form in the superficial portions of the piece, either before or after chromizing paths open to corrosion. Furthermore, the auxiliary components of the alloys form, with the diffused chromium, compounds which make the protection layer somewhat heterogeneous. This reduces the resistance of the piece to fatigue at high temperatures.

According to a feature of the present invention, the formation of such heterogeneous elements and the elimination of the metallic precipitates in the joints between the grains in the vicinity of the surface, while maintaining them inside the mass (which is necessary to achieve a good toughness at high temperatures) are avoided in the following manner:

Before the pieces of refractory material as above mentioned are subjected to the chromizing protective treatment, they are treated in such manner as to reduce the proportion of auxiliary elements in the superficial layer of said pieces. This treatment consists in first exerting a superficial oxidation of the pieces. This oxidizing superficially modifies the distribution of the auxiliary elements such as titanium and aluminum by causing them to diffuse toward the outside.

This layer of oxides is then removed.

The oxidizing treatment is performed by placing the pieces in the presence of an oxidizing agent such as air, either dry or moistened, iron oxide or the like, for a time which may vary, according to the composition of the alloy and the temperature of treatment, from some hours to some tens of hours, the temperature preferably ranging from 700° C. to a temperature close to the temperature of the first treatment of the alloy.

For practical purposes, the temperature must range from 800 to 1000° C.

As a result of this oxidizing treatment, there is formed a layer rich in chromium, titanium and aluminum oxides, formed at the expense of the amount of these metals existing in the superficial layers of the piece. The amounts of titanium and aluminum thus caused to form the superficial oxides are particularly high, due to the low percentage of these elements and to their high diffusion coefficients as compared to that of chromium.

This layer of oxides is removed preferably by a step which does not involve an attack of the alloy itself, for instance by an electro-thermic sodium scouring (electrolysis of melted sodium, the peices being placed at the cathode) or by a sodium hydride scouring.

The result can be still improved by subjecting the pieces, before the oxidizing, to a mechanical operation such for instance as a burnishing which produces a dislocation of the systems of heterogeneous precipitate so that the elements of said precipitates are more evenly distributed in the superficial layers which facilitate their diffusion toward the outside.

The pieces having thus been superficially freed from a portion of their auxiliary elements which cause the detrimental precipitates, in particular titanium and aluminium in the case of an alloy consisting chiefly of nickel and of the 80/20 modified Nimonic type, the chromizing operation is then performed.

The chromizing operation may be effected with a cementation mixture containing halides of metals which are to be introduced superficially, for instance chromium.

Furthermore, the pieces are advantageously surrounded by lumps of chromium for regeneration of the active vapors, the chromizing treatment taking place at temperatures ranging from 1050 to 1150° C. In this case, it is even possible to dispense with introducing chromium into the cementation mixture as the chromium halide is formed at high temperature indirectly by reaction of a metal halide on the regeneration chromium. In this case, the metal halide that is introduced is advantageously a halide of a metal existing in the alloy, for instance nickel chloride. In such a treatment, the elimination of the last traces of oxides that may have resisted to the preliminary elimination treatment takes place simultaneously.

Although this method can be applied to different kinds of refractory alloys consisting essentially of nickel and chromium, or of cobalt and chromium or of iron and chromium, it seems to be particularly interesting in the case of nickel and chromium alloys known as "modified 80/20 Nimonic type," these alloys containing the above mentioned auxiliary elements (such as titanium, aluminum, etc.).

Two examples of such an application of my method will now be given.

The first example is concerned with the treatment of a Nimonic 80 alloy (Cr 18.8%, Ti 2.4%, Al 1.4%, the remainder consisting of nickel and impurities).

The alloy was first oxidized for 15 hours at a temperature of 850° C. by means of dry air, then it was deoxidized by scouring in nascent sodium.

It was found that the composition of the alloy in the superficial layers had become as follows after this deoxidizing: Cr 18%, Ti 0.9%, Al 0.5%, which shows that the percentage of titanium and aluminum was considerably reduced.

This alloy was chromized in approximately gas-tight boxes heated in a hydrogen atmosphere by means of a cementation mixture consisting of chromium fluoride at 1080° C. for two hours. A rediffusion for six hours at 1080° C. lowered the superficial percentage of chromium from 60% to 38%.

The alloy was quenched in air then reheated for 16 hours at 700° C.

I thus obtained, in a layer of a thickness of about $^{10}/_{100}$ mm., a superficial layer enriched with chromium, of a hardness lower than that inside the mass of the alloy, ductile and very homogeneous.

The second example is concerned with the treatment of a Nimonic 90 (Co 20%, Cr 19%, Ti 2.8%, Al 1.4%, the remainder consisting of nickel and impurities).

The alloy was superficially oxidized for 10 hours at 900° C. by means of moist air. The composition of the alloy in the superficial layer thereof, after deoxidizing by means of nascent sodium became: Cr 17%, Ti 0.8%, Al 0.6%.

This alloy was chromized in an atmosphere free from nascent nitrogen (in approximately gas-tight boxes heated in a hydrogen atmosphere) by means of a nickel chloride indirect cementation mixture, the pieces being surrounded by particles of regeneration chromium. The cementation mixture was placed out of contact with the pieces in treatment. The chromized layers thus obtained contained a lower percentage of chromium so that the rediffusion operation could be dispensed with.

The chromizing operation was performed during the eight hours of the initial treatment at 1080° C. The alloy was quenched in air, then reheated for 16 hours at 700° C.

The superficial layer, containing a suitable amount of chromium (average percentage of about 30%) was perfectly homogeneous.

A Nimonic 80 was treated as above stated (oxidizing followed by scouring). The pieces were chromized in approximately gas-tight boxes heated in a hydrogen atmosphere with a cementation mixture consisting of 25% chromium fluoride and 75% nickel chloride, said pieces being surrounded by particles of regeneration chromium for two hours at 1080° C. A rediffusion treatment for two hours at 1080° C. lowered the superficial percentage from 45 to 32%.

Another feature of the invention which is independent of those above described will now be described. This feature relates to the case where the refractory alloy to be superficially chromized contains carbon either free or in combination. In this case, this carbon tends during the chromizing operation to diffuse toward the surface of the piece, possibly after having been displaced from its combination and to form, with the excess of chromium present in the superficial layer, chromium carbides which deposit in the joints between metallic grains and thus facilitate corrosion of the piece.

In order to avoid this drawback, according to the present invention, there is diffused into the pieces, during the chromizing operation, together with chromium at least one metal having higher affinity than chromium with carbon. This metal gives carbides which precipitate inside the grains and no longer along the joints. Such a metal may consist in particular of zirconium, titanium, molybdenum, tungsten or manganese.

Zirconium and titanium may advantageously be introduced into the cementation mixture used for the chromizing operation and which contains fluoride compounds. These metals (i. e. zirconium and titanium) are introduced in the form of oxides (ZrO_2 or TiO_2) which would react upon the fluoride of said cementation mixture according to endothermic reaction which takes place gradually and is balanced, this reaction starting only at temperatures of about 700–800° C. These oxides are preferably mixed with the regeneration chromium mass in the form of a diluting substance, thus serving to support heavy pieces in the treatment container. The zirconium or titanium fluorides that are thus formed have a favorable action upon the homogenizing of the atmosphere. But if such fluorides are placed directly in the cementation mixture (or if zirconium or titanium was placed directly therein), there would be an intensive disengagement, even at low temperatures, which would be unsuitable for a good treatment.

Molybdenum and tungsten may also be introduced into the fluorine containing cementation mixture in the form

of oxides (MoO_3 or WO_3) which react similarly with chromium fluoride so as gradually to form active molybdenum and tungsten oxides.

Molybdenum and tungsten may also be introduced directly in a cementation mixture containing ammonium fluoride. It is also possible to add to a chromium cementation mixture an ammonium compound of one of these metals (for instance $(NH_4)_2WO_4$).

Molybdenum and tungsten fluorides are also very good homogenizing agents.

As for manganese, it may be introduced into the cementation mixture in the form of oxide MnO_2 or mixed directly with the ammonium fluoride.

By way of example, sheets of Nimonic 75 may be chromized with a cementation mixture containing titanium oxide, the treatment then taking place only for one hour (after heating up), and titanium oxide is advantageously added with the regeneration mass of chromium for supporting the Nimonic sheets.

Resistor wires may be chromized in the presence of a cementation mixture containing one or several zirconium, titanium, molybdenum oxides, and possibly alumina.

What I claim is:

1. A method for treating a refractory alloy piece including mainly a primary metal selected from the group consisting of iron and nickel and also a secondary metal selected from the group consisting of chromium, molybdenum, cobalt, aluminum, titanium and manganese in sufficient quantity to impart refractory properties to said alloy comprising diffusing chromium into the surface layer of said piece by chromizing with chromium fluoride vapors sufficiently long to form a solid solution of chromium in said layer in said primary metal capable of precipitating chromium compounds on cooling said piece and subsequently heating said diffused piece in an environment consisting mainly of hydrogen to cause rediffusion of chromium further into the mass of said piece until the amount of chromium in said surface layer is lowered sufficiently to prevent precipitation of chromium compounds on cooling.

2. A method according to claim 1 wherein chromium is the sole metal diffused into said piece.

3. A method according to claim 1 wherein said piece is diffused with chromium and a third metal selected from the group consisting of aluminum, silicon, zirconium, titanium, tungsten, manganese, vanadium and molybdenum.

4. A method according to claim 1 wherein after said rediffusion said piece is quenched in an oxidizing bath and is subsequently heated briefly in an atmosphere of chromium halide vapors at a temperature high enough to totally reduce the oxide layer formed as the result of said quenching and below that causing a substantial diffusion of chromium into said piece.

5. A method according to claim 1 wherein during said rediffusion said environment is free of carbides and compounds capable of producing nascent nitrogen.

6. A method according to claim 1 wherein the method is carried out within a substantially gas-tight container heated in a hydrogen atmosphere, said container having therein a cementation mixture capable of producing said chromium fluoride vapors on heating, and exhausting said chromium fluoride vapors prior to said rediffusion.

7. A method according to claim 1 in which said piece is thin and prior to said diffusion can be shaped but cannot be shaped after said rediffusion.

8. A method according to claim 7 wherein said piece has a maximum wall thickness of 2 mm.

9. A method according to claim 7 wherein said piece has a maximum wall thickness of 3 mm. and is diffused with chromium and a third metal selected from the group consisting of aluminum and silicon.

10. A method according to claim 1 wherein said piece contains carbon and is diffused with chromium and a third metal having a greater affinity for carbon than chromium and selected from the group consisting of zirconium, titanium, molybdenum, tungsten, manganese, and vanadium whereby carbon and said third metal precipitates in the grains of said piece.

11. A method according to claim 1 wherein said piece contains carbon and is diffused with chromium and silicon whereby said silicon forces said carbon toward the interior of said piece.

12. A method for treating a refractory alloy piece composed mainly of a primary metal selected from the group consisting of iron and nickel and also a secondary metal selected from the group consisting of chromium, molybdenum, cobalt, aluminum, titanium and manganese in sufficient quantity to impart refractory properties to said alloy comprising exposing said piece in a container at a chromizing temperature range to chromium fluoride vapors evolved in said container from a cementation mixture therein capable of producing chromium fluoride vapors on heating, said exposure being sufficiently long to form a solid solution of chromium in the surface layer of said piece in said primary metal capable of precipitating chromium compounds on cooling said piece, subsequently heating said cementation mixture to completely vaporize said chromium fluoride, condensing said chromium fluoride vapors and maintaining said condensate as such in a cooled first portion of said container, and subsequently heating said chromized piece in a second portion of said container spaced from said first portion in an environment consisting mainly of hydrogen to cause rediffusion of chromium further into the mass of said piece until the amount of chromium in said surface layer is lowered sufficiently to prevent precipitation of chromium compounds on cooling.

13. A method for treating a refractory nickel-chromium alloy piece containing a secondary metal selected from the group consisting of titanium and aluminum which form precipitates in said alloy and achieve structural hardening thereof comprising oxidizing said piece to cause said secondary metal to diffuse toward the surface, removing the layer of oxides formed thereby, diffusing chromium into the surface layer of said piece by chromizing with chromium fluoride vapor sufficiently long to form a solid solution of chromium in said layer of said alloy capable of precipitating chromium compounds on cooling said piece and subsequently heating said diffused piece in an environment consisting mainly of hydrogen to cause rediffusion of chromium further into the mass of said piece until the amount of chromium in said surface layer is lowered sufficiently to prevent precipitation of chromium compounds on cooling.

14. A method according to claim 13 wherein said oxide layer is removed by scouring so as not to attack the mass of said piece.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

February 24, 1959

Patent No. 2,875,090

Philippe Galmiche

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 18, for "peices" read -- pieces --; column 4, line 43, for "55.60%" read -- 55-60% --; column 7, line 26, for "leasting" read -- lasting --; column 10, line 57, for "fluoride" read -- fluorine --.

Signed and sealed this 30th day of June 1959.

(SEAL)

Attest:

KARL H. AXLINE

Attesting Officer

ROBERT C. WATSON

Commissioner of Patents