## ALIEN PROPERTY CUSTODIAN

CEMENTATION OF METALS AND METAL ALLOYS WITH BERYLLIUM

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The present invention relates to improvements in or relating to the cementation of metals and metal alloys with beryllium.

It is an object of the invention to cement with beryllium, objects produced from metals such as iron, for example cast iron, steel, normalized steel and the like, further objects produced from metals such as copper, silver, nickel, aluminium and the like and from metal alloys of the most varied kind, for example bronzes and the like.

It is known that beryllium reacts extraordinarily readily with all kinds of compounds and substances, especially with oxygen and nitrogen, and with steam, carbon dioxide and the like. Because of this property of beryllium, it was to be 15 expected that satisfactory cementations would only be obtained if it were possible to protect the beryllium adequately during the heat treatment. Experiments in which a metallic object to be cemented was packed in pulverulent beryl- 20 lium in order to protect the beryllium particles, which lie upon the metal surfaces to be cemented, by the layers disposed thereabove have not led to satisfactory results. In any event this process is impracticable because of the relatively high price of beryllium.

It has now been found that excellent cementations may be obtained if a thin layer of beryllium is applied to the surfaces to be cemented and the beryllium caused to diffuse into 30 the base metal by heating. It has been shown that with this method of working diffusion of beryllium into the base metal takes place so rapidly and completely that in spite of the great carbon dioxide and the like disturbing reactions do not take place.

The beryllium, when applied in a thin layer. may surprisingly be caused to diffuse completely into the base metal considerably more rapidly 40 than when it is applied by the above mentioned packing process. This ability to induce rapid and complete introduction with complete utilisation of the expensive beryllium employed and to obtain very uniformly cemented products is of 45 erably between about 850 and 1000° C. considerable technical and economic importance. Objects cemented with beryllium by the above process are distinguished by very hard surface layers and particularly high resistance to mechanical influences, temperature influences and 50 the like. In fact effects may be obtained which are not obtainable by known cementation processes.

It is also, inter alia, an advantage of the proc-

lable manner and thus makes it possible to produce products of desired properties. For example, the quantity of beryllium to be introduced into the base metal may be exactly predetermined by choice of the thickness of the beryllium layer applied to the base surface. Moreover, a more or less deep penetration of the beryllium into the base metal or, for example, the production of surface layers of desired degree 10 of hardness may be obtained very simply by temperature regulation. For example by applying relatively thin beryllium layers and employing relatively high temperatures, a thin surface layer of great hardness may be obtained. Moreover, for example by employing thicker beryllium layers and observing relatively high temperatures, surface layers may be obtained which are not only very hard but are also distinguished by great resistance to mechanical influences. temperature influences and the like. Greater depth effects may for example be obtained by use of thicker beryllium layers and relatively low temperatures. Further controls are, for example, available by carrying out the cementation 25 in steps at temperatures of various heights, for example first at relatively lower and then at relatively higher temperatures. Variations may also be obtained by employing various periods of heating or temperatures of various height with periods of heating of various lengths. A further possibility consists, for example, in first allowing a beryllium-containing layer to diffuse in, thereupon applying a further layer, allowing the latter to diffuse in by heating and if desired repeataffinity of beryllium for oxygen, nitrogen, steam, 35 ing this process frequently. In this way great depth effects may for example be obtained with only very gradual transitions and hence particularly homogeneous and resistant cementation layers may be produced.

The heat treatment should be carried out at temperatures at which a disturbing fusion of beryllium or of the base metal does not take place. Suitable cementation temperatures lie principally between about 800 and 1100° C., pref-

The heat treatment may advantageously be carried out in vacuo or in an atmosphere of inert gas, for example in an atmosphere of hydrogen or of the rare gases, such for example as argon. The heating may be effected by methods known per se, for example by means of hot gases, radiant heat, Joule heat, turbulent current heating or in fused salt baths. The process may also for example be such that only the first part of the ess that it may be carried out in a readily regu- 55 heat treatment is carried out with exclusion of

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aggressive gases, whilst further diffusion may be effected without these precautionary measures.

Beryllium coatings may for example be produced on the base metal by incorporating beryllium in as finely divided as possible a form in lacquers or similar media such, for example, as resins, artificial resins and/or other vaporisable or combustible substances or mixtures of substances and applying the products so obtained to 10 the base in suitable manner. Suitable lacquers are for example those having a base of cellulose esters, artificial resins, rubber, resinates, oil lacquers and the like. Known solvents, softening resins and the like. The usual measures such as dipping, spreading and spraying may be employed for the application of the substances or mixtures of substances containing the beryllium in suspension.

The beryllium may also be applied to the base in admixture with inert, fusible substances, such, for example, as calcium fluoride.

Application of the beryllium as a component of the sprayable, dippable or spreadable lacquers 25 and the like makes possible, in particular, uniform cementation of complicated space structures, such as armatures, large apparatus parts and the like.

In many cases it has proved advantageous to 30 roughen up the base metals superficially by means known per se, for example by means of sand jet blasts, etching liquids or electrolytically. A somewhat lattice-like form may for example be imparted to the surfaces. The application and 35 adhesion of the beryllium or of the berylliumcontaining products such as lacquers or the like, and the subsequent diffusion into the metal may be favoured by employing surfaces of this kind. It has been found that the beryllium may also be 40 caused to adhere sufficiently to the base metal on such rough surfaces without use of binding agents and the like, for example by powdering in, pressing in and the like.

are suitable for applying the beryllium in a uniform and sufficiently adhesive layer to the base metal, such for example as the metal spraying process which is particularly suitable for the treatment of large metal objects.

According to one embodiment of the invention, other metals or metal alloys besides beryllium are also caused to diffuse into the base metal. In this way it is possible extensively to influence the properties of the cemented surfaces of the 55 base metal in desired directions. Suitable additional cementation agents for the cementation of iron, steel, normalized steel and the like, are for example copper, nickel, tungsten, titanium, vanadium, aluminium and the like. The beryl- 60 lium may be applied to the base metal together with suitable quantities of additional metals, for example by powdering on or pressing on to roughened surfaces or, for example, in the form of lacquers or the like. If desired thin layers of 65 beryllium and of additional metal, for example copper, may also be applied alternately to the base metal. In this case the layer last applied advantageously consists of the additional metal, for example copper, and in this way the beryllium 70 is provided with a protective coating. Finally the beryllium may also be applied to the base in the form of alloys which contain the additional metal or the additional metals.

beryllium and also the additional metal or the additional metals diffuse into the base metal; according to the quantitative relation of the metals introduced and also the sequence of introduction and the like, special effects may be obtained.

According to another embodiment of the invention, besides beryllium or beryllium and additional metals, other cementation agents such, for example, as coal, silicon and the like are also caused to diffuse into the metal to be treated.

This may for example be effected in a simple manner by applying the beryllium to the base metal together with components which are caragents and the like may be added to the lacquers, 15 bonised on heating, for example in the form of lacquers, or by adding carbon, silicon or like components in suitable quantitative proportions to the beryllium or the beryllium-containing mixtures.

> According to a further embodiment of the invention a beryllium compound or beryllium compounds is/are applied to the base metal, or a coating is applied which contains a beryllium compound or several beryllium compounds, the beryllium is then set free from its compounds and caused to diffuse in.

> Thus, for example, organic beryllium compounds, such, for example, as beryllium dimethyl, or beryllium diphenyl, may be vaporised and precipitated onto the surface of the metals or metal objects to be improved. If in this case the base metal is maintained at suitably high temperatures, the metallo-organic compound decomposes and precipitates finely divided beryllium which is introduced into the base metal by further heating to temperatures suitable for the diffusion in of the beryllium.

If desired also a mixture containing a reducible beryllium compound for example beryllium oxide, beryllium chloride, beryllium fluoride and the like, and a suitable reducing agent, may be applied as a coating to the base metal, the reduction of the beryllium compound may then be effected by heating and the beryllium set free may be Of course there are other possible ways which 45 caused to diffuse into the base metal by further heating.

> As reducing agents, metals may advantageously be employed which are capable of forming alloys with the metallic beryllium set free.

> Thus for example, the base metal may be provided, for example electrolytically, with a coating of strongly electropositive metals, such, for example, as sodium, magnesium, aluminium or calcium, the beryllium compound, for example beryllium chloride, may then be applied, if desired in admixture with other suitable substances, for example alkali chloride or other suitable fluxes, preferably in a reducing atmosphere, and heated to produce complete or partial reduction of the beryllium compound to metallic beryllium. The beryllium set free is then caused to diffuse practically completely into the base metal by heating, the process being controlled if desired as described before.

> If desired also the base metal may be coated with the reducing agents and then treated at higher temperatures with beryllium compounds in vapour form, for example with beryllium halides and the beryllium set free caused to migrate into the base metal by increase of temperatures.

The reducing agent, for example magnesium or aluminium, may be employed in such quan-On heating to suitable temperatures, both the  $_{75}$  tities that it is present in more or less great

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excess and diffuses in together with the beryllium.

Other metals, such, for example, as copper, nickel, cobalt, silver etc. may also be introduced besides the beryllium into the base metal and in this way the properties of the surface layers cemented by beryllium may be varied in desired manner. For example, a coating of more noble metals, for example copper, nickel, cobalt, silver, may first be applied electrolytically to the base 10 metal and likewise a coating of less noble-metals, such as magnesium or calcium, may be applied electrolytically to this first coating. Thereupon a suitable compound yielding metallic beryllium, for example beryllium chloride, may be applied 15 in the above described manner. Reduction of the beryllium compound to metallic beryllium and alloying of the beryllium metal with the other metal, for example copper, may be effected by heating, and the alloy produced may then be caused to diffuse into the base metal by further heating.

The beryllium compound yielding metallic beryllium for example beryllium chloride, may also be applied in admixture with reducing substances other than those above mentioned, for example in admixture with coal, carbides or hydrides of the alkali or alkaline earth metals. In this case, besides beryllium and if desired also other metals, cementation agents of another kind such, for example, as carbon, may also be introduced into the base metal and special effects may be obtained, for example, as regards hardness.

vided with a coating of lacquers or the like containing the beryllium compound, the additional substances necessary for setting free the metallic beryllium and if desired also other additions, for example other metals or coal or silicon 40 and the like. For example a desired lacquer having a basis of cellulose esters, resins or artificial resins, varnishes, softening agents, solvents and the like may be mixed with beryllium oxide or beryllium chloride and suitable reducing agents, for example finely divided magnesium, calcium etc.; moreover other substances such, for example, as coal, finely divided metals, such for example as copper, nickel and the like, or

compounds suitable for giving such metals, for example oxides capable of reduction under the given conditions may be incorporated with the lacquer. Such lacquers may be applied to the metal object to be improved, for example by spreading, dipping or spraying. Thereupon the lacquer substance is advantageously heated in an inert or reducing atmosphere until decomposition of the lacquer substance takes place, whereupon the temperature is raised to the degree necessary for the reduction of the beryllium compounds and if desired of other metal compounds and if desired for the alloying of the beryllium with other metallic components, and the beryllium and if desired other substances to be introduced in the base metal are caused to diffuse in by heating to suitable temperatures. Working with lacquers and like products is particularly suitable for improving apparatus parts, armatures and the like of complicated constructions, and especially for improving hollow spaces which can be coated with the lacquer, for example by spraying or like measures.

Objects such, for example, as plates with level surfaces may advantageously be improved by applying the beryllium in a layer of suitable thickness to the surface of a plate laying a corresponding second plate thereupon and subjecting the plates thus united with one another to a common heat treatment. It is thus possible to cause the beryllium or also mixtures of beryllium with additional components to diffuse into the surface of the two plates simultaneously. It is moreover an advantage of this procedure that The base metal to be improved may be pro- 35 the beryllium is protected against the influence of air and other disturbing gases so that it is not necessary to employ special measures for excluding air and other disturbing gases. It is advisable when working in this way to take precautions to ensure as intimate as possible a contact by pressing together the plates, sheets and the like.

> The diffusion in the beryllium and if desired also of other cementing or otherwise favourably acting substances by heat treatment may advantageously be induced in most of the embodiments described by using baths of fused liquids.

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