May 18, 1971 V. J. PINGEL 3,579,373

CARBIDING

Filed Oct. 18, 1968

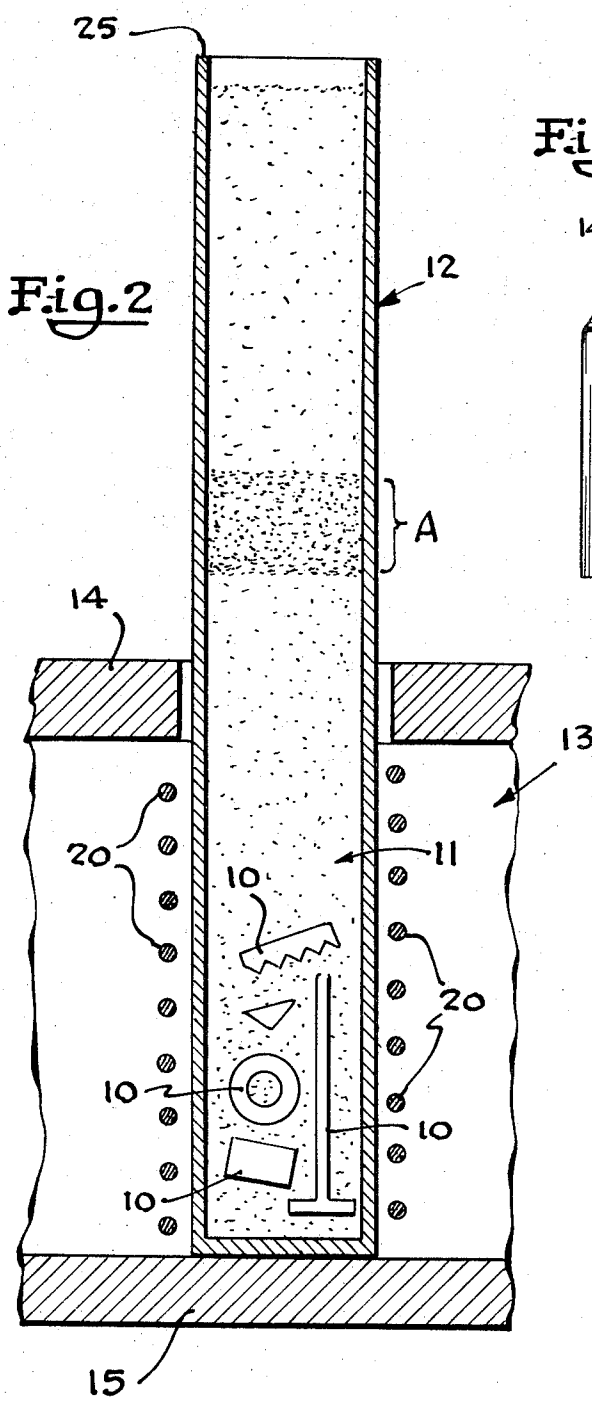


Fig.2

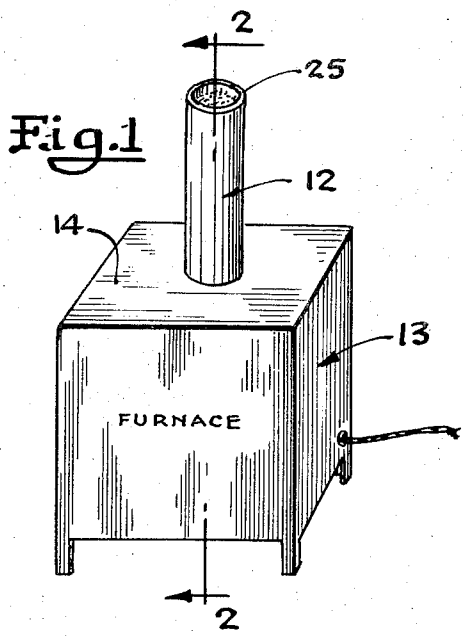


Fig.1

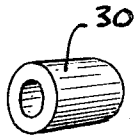


Fig.3



Fig.4

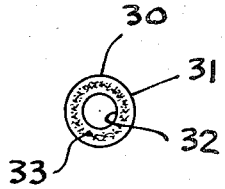


Fig.5

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CARBIDING

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ABSTRACT OF THE DISCLOSURE

A method of applying a carbide coating to a surface of an article having 0.5% or more carbon which includes imbedding the article in a packed bed which has an upper portion at a lower temperature and in communication with the atmosphere, the condensible volatiles moving from the high temperature lower portion condense in the upper portion and are prevented from being moved into the atmosphere. The ingredients of the pack include an anti-fusing agent, a metal source component, halide of the metal source component, and barium chloride.

BACKGROUND OF THE INVENTION

Altering the surface of metal such as steel and non-metals such as carbon or graphite articles to provide an extremely high degree of hardness and abrasion resistance is of great commercial significance. It has been suggested that a layer of chromium be deposited on metals by methods which are commonly known as "vapor deposition" methods. These methods usually involve depositing a layer of chromium on the surface of a metal article while residing in an inert atmosphere, reducing atmosphere, vacuum, or in a molten bath. These methods are generally cumbersome. They are not entirely suitable for use in foundry-like conditions which require extreme simplicity in procedures. These methods lead to the deposit of chromium which alloyed with the iron base almost immediately. Also, the materials used in the methods heretofore suggested were often difficult to handle, and losses of these materials in the course of operation tended to be expensive. It is an object of the present invention to provide a method for depositing an extremely hard carbide layer on the surface of articles using a reusable powder bed which can be operated in simple equipment while it is exposed or vented to the room atmosphere. It is a further object of this invention to provide a method for depositing a carbide layer on carbon articles, e.g. graphite, as well as on articles which contain relatively small amounts of carbon, e.g. 0.5% and above. It is an important object of this invention to provide a method for producing carbide coatings which method involves virtually no loss of ingredients.

SUMMARY OF THE INVENTION

This invention relates to a method of depositing carbide coatings on articles containing 0.5% or more carbon at the surface thereof. The method involves the use of a powdered bed confined in equipment having a first and second region. The article is imbedded in the bed in the first region and this region of the bed is heated to a temperature of insipient fusion of the bed. A second region of the equipment is located between the heated first portion and the atmosphere even though the bed is in direct pneumatic communication with the atmosphere through the second region. The second region of the equipment is maintained at a temperature below the temperature at which condensible volatiles moving from the heated region are condensed. The only pneumatic communication between the bed and the room atmosphere is through an orifice above the second region, a sufficient height to prevent passage of condensible volatiles into the atmosphere,

and to maintain protective heavy volatile condensibles between the room atmosphere and the heated bed during the process. The rate and quality of deposition on the article can be altered by application of an external electrical potential to the article.

DESIGNATION OF THE FIGURES

FIG. 1 is a perspective schematic view showing a tube in place in an electric furnace;

FIG. 2 is an enlarged schematic cross-sectional view taken approximately along the lines 2—2 of FIG. 1;

FIG. 3 is a perspective view of a cylindrical article which was carburized and then sawed off from the remaining portion of the cylindrical article prior to treatment in accordance with this invention;

FIG. 4 is an end view of the article shown in FIG. 3 as viewed towards an end which has been carburized prior to treatment in accordance with this invention; and

FIG. 5 is an end view of the article shown in FIG. 3 as viewed towards the end exposed by sawing the carburized article through prior to treatment in accordance with this invention.

DESCRIPTION OF PREFERRED EMBODIMENTS

Although the following disclosure offered for public dissemination, in return for the grant of a patent, is detailed to ensure adequacy and aid understanding, this is not intended to prejudice that purpose of a patent which is to cover each new inventive concept therein no matter how others may later disguise it by variations in form or additions or further improvements. The claims at the end hereof are intended as the chief aid toward this purpose; as it is these that meet the requirement of pointout out the parts, improvements, or combinations in which the inventive concepts are found.

In accordance with this invention articles **10** which contain 0.5% or more carbon are imbedded in a bed **11** of powder, the makeup of which will be described in greater detail herein. The powder bed is contained in a suitable vessel, or tube **12** (e.g. one made of Inconel, ceramic, or other suitable material). The bed-containing tube **12** is placed in a furnace **13** in such a manner that the tube may be considered as having two regions, namely the lower portion containing the bed that is being heated, and the upper portion containing the bed that resides outside of the furnace and is thus maintained at temperatures far below the temperatures encountered within the furnace. Thus the first portion of the bed, which may be defined approximately as that portion between insulated top **14** and insulated bottom **15**, is subjected to the heating action of heating elements **20** in furnace **13**. This portion of the bed is heated to a temperature of insipient fusion. The meaning of this term will be explained more fully hereinafter. After the operating temperature is reached in the heated portion of the bed certain condensible volatiles are formed and flow through the voids in the powdered bed. The condensible volatiles move upwardly in the illustrated embodiment to the second region in which the tube and the bed are not heated. In this region, particularly in the approximate region marked A in FIG. 2, the condensible volatiles are condensed. The bed in the region marked A becomes a readily friable, integral mass. In a preferred embodiment the portion of the bed which is maintained at condensing temperatures, i.e. in the second region of the equipment is sufficiently large to assure complete condensation in the bed of the condensible volatiles formed in the heated portion of the bed. Naturally as the heating period is prolonged a greater and greater quantity of condensibles are collected in the region designated A in FIG. 2 and in many instances the quantities of material become large enough to virtually plug the bed, i.e. sever the pneumatic communication between the cooled upper

and heated lower portions of the bed. In a less preferred embodiment the bed does not extend into the second, cooled region, and condensation takes place on the walls of the vessel in the stagnant atmosphere of that region of that vessel.

Even if a plug does not form in the cooled region of the bed, the heavy gases or volatiles can rise a limited extent in the cool region, thus giving adequate protection to the "atmosphere" in the hot zone. In accordance with this invention it is essential that the direct pneumatic communication or orifice between the confines of the vessel and the room atmosphere be at a sufficiently high vertical distance above the heated portion of the bed that the apparent uppermost level of volatiles formed does not reach the orifice of the vessel at any time during the process.

BED MAKEUP

The bed employed in accordance with this invention is made up of finely divided, preferably powdered, ingredients consisting of four components. The first component is an anti-fusing component and is selected from materials which retard or inhibit sintering or fusing of the remaining components. The first component is selected from materials which do not melt or become sticky at operating temperatures. Examples of classes of materials from which the first component may be selected are alundum, or other aluminum oxide materials, crushed firebrick, ceramics, etc. The first component is present in an amount between 5% and 70% inclusive, preferably 5%–50%.

The second component is a metal-source component and is selected from the group high carbon or low carbon ferrochromium, chromium, ferro-molybdenum, molybdenum, ferrotitanium, titanium, ferrotantalum-columbium, ferro-columbium, ferro-tungsten, and tungsten. The metal source component is used in an amount between 5%–80% inclusive of the bed preferably between 5% and 50% inclusive of the bed by weight.

The third component is a metal halide in which the metal is one of the metals present in the metal source component, for example, chromium chloride ($CrCl_3$). The metal halide component is used in an amount between about 5% and about 70% by weight of the bed preferably between 7% and about 30% of the weight of the bed.

The fourth and also essential component is barium chloride. This component is used in an amount between 7% and 80% by weight of the bed more preferably between about 10% and 80% of the weight of the bed.

I believe that the metal-source component contributes substantially also to the heat conductivity of the bed, and therefore I prefer to use ratios of ingredients which have a high metal-source component level. I also prefer to use a minimum amount of the first, anti-fusing, component consistent with safe operation of the bed. I believe that such low levels of the anti-fusing component permits maximum involvement of components actually involved in the generation of the coating. I have found that ferrochromium silicon, which is generally recognized by the art to be non-equivalent to ferrochromium cannot be used in the method of this invention. Beds in which ferrochromium silicon is used have an extremely short useful life after which they become inactive with respect to forming the carbide coating. Also, it is essential that halides of the metals involved be present. The substitution of chromium oxide (Cr_2O_3) for chromium chloride does not result in a useful bed.

However, some of the barium chloride can be replaced by melting point depression agents, such as sodium chloride or potassium chloride, (e.g. 10% to 50% by weight of the barium chloride) for the purpose of lowering the fusion temperature of the salt. However, it is essential that the barium chloride be present in amounts as stated above. Elimination of the barium chloride from the ingredients of the bed results in a mixture which is not useful in accordance with this invention.

In this specification, and in the definition of the method of this invention the term "temperature of insipient fusion" is used. This term indicates not a single temperature but a range of temperatures which is above the melting or sintering temperatures of some of the ingredients of the bed and yet is below the temperature at which the bed will fuse or sinter and lose its identity as a powder or readily friable mass. Thus in a bed consisting of 33.5% alundum, 33.5% ferrochrome, 16.5% barium chloride and 16.5% chromium chloride temperatures between 1700 and 2000 are in the range of temperature of insipient fusion, particularly temperatures in the range 1800 to 2000. The temperature of fusion of a mix can be readily determined experimentally by a simple test which consists of placing a number of samples in a furnace and gradually raising the temperature of the furnace while removing samples periodically. After cooling, the samples are subjected to light tapping and those samples which have not yet reached the temperature of fusion will readily disintegrate and return to the powder condition. On the other hand, samples which have reached the fusion temperature solidify into an integral mass which can no longer be considered readily friable. While I do not want to be bound by any theories it is my understanding that the fusion of the bed into an integral mass as a result of exceeding the temperature of fusion of the bed involves the results of melting or sintering, or both, of the ingredients.

While both high and low carbon ferrochromium will work in accordance with this invention, high carbon ferrochromium, e.g. ferrochromium containing 65%–70% chromium and 4%–9% carbon, the balance being iron, is preferred. However, it appears that low carbon ferrochromium generally gives a higher shine coating than the high carbon ferrochromium.

The source-metal halide can be added to the other ingredients of the bed as an aqueous solution, but the resulting wet mixture must be dried prior to use as a coating bed or severe metal corrosion may result. However, the application of the chromium chloride to the remaining ingredients by way of a concentrated chromium chloride aqueous solution followed by drying of the wet ingredients produces a highly reactive bed mixture. However, the practical difficulties encountered due to the corrosiveness of the aqueous chromium chloride are generally not sufficient to justify this method because of the increase in reactivity. Consequently, simple admixing of the components in the form of dry powdered ingredients is generally the most practical and suitable in foundry-like operations.

Molybdeum carbide can be applied as a coating if ferromolybdeum, or molybdeum is employed as metal source with molybdeum chloride. It is preferred that the metal source component be 55%–75% Mo, 0.1 to 2.57 C, balance being iron.

Tungsten carbide is applied if ferro-tungsten (e.g. 65%–82% tungsten, .25 to 2.50% carbon, balance iron), or tungsten is used in conjunction with tungsten chloride.

Tantalum carbide can be coated if pure tantalum is used; or tantalum and columbium carbides can be coated in accoradnce with this invention if a metal source such as ferro-tantalum-columbium (20% Ta, 40% Cb, .20% C, bal. Fe) or ferro-columbium (58% to 62% Cb, bal. Fe) is emploeyd, with tantalum chloride and/or columbium chloride.

Titanium carbide can be applied by use of ferrotitanium (e.g. 15%–20% titanium, 1%–2% aluminum, 2%–3% silicon, 3%–8% carbon, balance iron) or titanium in conjunction with titanium chloride.

While I do not want to be bound by any theories it is my belief that the metal-source component resupplies the metal chloride with the metal ions that are taken from volatile chloride as it reacts to form the carbide coating. It is my understanding and belief that chromium chloride

vapor ($CrCl_2$) is present in the voids in the heated portion of a bed containing $CrCl_3$ powder.

CARBON CONTENT OF ARTICLES

I have found that the carbide coating can be incorporated on the surface of articles which contain 0.5% carbon or more, or on articles which have a carbon coating thereon. Thus, steels such as 1020 steels (0.20% carbon) are not suitable for use in accordance with this invention. However steels such as the 1060 and the 52100 steels (0.60% and 1.00% carbon, respectively) are entirely satisfactory for use in accordance with this invention.

Likewise, I have discovered that painting or printing ceramics or other objects, such as copper sheets, with a carbon-containing or graphite-containing ink provides a surface which can be carbided in accordance with this invention. One such "ink" is "DAG" (trademark of Atchison Colloidal Graphite Company) which is a colloidal suspension of graphite in a suitable carrier such as kerosene, water, alcohol, etc. or in admixture with a grease-like material. Subjecting an article imprinted with such a material to the process of this invention results in a deposition of a metal-like coating in the areas in which the printing occurred. While I do not want to be bound by any theories it is my understanding and belief that the operating temperatures of the method of this invention, being just below the melting point of copper, causes a carbide coating formed by reaction with the carbon imprintation on copper to be diffused and fused into the copper underlayment. Thus, it will be appreciated that not only is this method highly useful in the fine arts, but it is also of considerable use in the preparation of etching, etc. The high chemical resistance of the carbide coating is utilized to permit selective dissolution of the uncoated copper underlayment leaving the carbide coated regions substantially unaffected. Such etchings have unusually hard elevated surfaces.

On the other hand articles made of graphite can be partially shielded from the application of a coating in accordance with this invention by electroplating a fine copper coating on the area to be protected and subsequently treating the entire article in accordance with this invention. The result is that the carbide coating is not laid down over the copper layer but is laid down on the unprotected regions of the carbon or graphite article. The examples presented hereinafter will further illustrate the importance of the proper carbon level in the method of coating articles in accordance with this invention.

In the examples and throughout the specification the reference to percent (%) are percent by weight, and parts is expressed in parts by weight. Also, all references to temperatures are expressed in degrees Fahrenheit.

Example 1

A number of articles **10** having the carbon contents set forth in Table I were placed in a bed **11** having the following makeup: alundum (33.5%), ferrochrome (33.5%), chromium chloride ($CrCl_3$, 16.5%), barium chloride ($BaCl_2$, 16.5%). (The bed was 100%–6 mesh, 90%–20 mesh.) This bed **11** and articles **10** are placed in the loweremost portion of an Inconel tube **12** which is closed at the lowermost end. Additional outer material having the same makeup as the first portion of the bed is added to fill the elongated Inconel tube to within a few inches of the open end **25** of tube **12**. Tube **12**, thus charged, is placed vertically in a suitable furnace **13** which is constructed to heat only the lowermost portion of the charged tube which confines the portion of bed **11** in which articles **10** reside. The uppermost portion of the tube extends outside of the furnace and is maintained at relatively low temperatures, due to the cooling effect of the room atmosphere. Furnace **13** is energized to heat tube **12** and the lower region of its contents as rapidly as possible to a temperature of about 1900 degrees F. This took approximately one hour. The tube and its contents were maintained in the furnace at 1900° F. for two additional hours. At the end of the two hours the tube was removed from the furnace and was permitted to air cool to room temperature. The tube was inverted and the extreme topmost portion of the bed poured readily from the tube. However, a plug was found approximately one-half way down the depth of the tube approximately in the region marked A in FIG. 2. This plug disengaged itself from the tube when the tube was tapped lightly and the remaining portion of the contents poured readily from the tube. The plug was readily friable and slight pressure returned the plug to a relatively powdery condition. The results of the demonstration are tabulated in Table I below.

TABLE I

Article	Carbon, percent	Result
Armco ingot, iron	0.00	Unacceptable as a coating, metal appeared corroded, surface extremely mottled, Rockwell hardness, ranged C 20 and downward.
Steel:		
1020	.20	
1040	.40	
1060	.60	Shiny, hard (C 72) suggestive of mottled character.
1090	.90	Smooth, hard, very shiny.
52100	1.00	Smooth, hard, appears polished.
Cast iron	2.00	Smooth, hard, shiny coating.
Pure carbon (amorphous)	100	Coating has white, lustrous appearance, depending on condition of undercoat.
Graphite	100	

Thus it is seen from the data of Table I that materials containing less than 0.5% carbon were not given a chromium carbide coating in accordance with this invention. Materials having 0.6% or more carbon exhibited a shiny, hard carbide coating after treatment in accordance with this example.

Example 2

Articles fabricated from a high carbon, high chrome steel known as crucible "Air-Kool" steel were imbedded in a series of beds having the same makeup as that set forth in Example 1 above and each bed was subjected to the conditions set forth in Example 1 above except that different size beds and furnaces were employed. At the end of the two hour uniform temperature heat treatment period, the furnaces were shut off and the tubes were permitted to remain in the furnaces while the furnaces cooled to room temperature. Upon removal of one of the tubes after the cooling period was completed it was found that the core of the articles had a martinsitic structure. In the tests in which a small furnace and a small (1½ inch diameter) tube were employed the cores were very hard, and brittle, and the coating was a hard and brittle coating. These materials are heated to temperatures of 400° F. to 1000° F. depending on the composition of the steel and permitted to cool in air. This heat treating step resulted in a tough core with the hard case of chromium carbide remaining unaffected.

When a large bed is employed in a large furnace in the procedure of this example, so that the cooling period is a prolonged one, the result is that the core is annealed, i.e. relatively soft and flexible. Yet the article has an extremely hard case. These articles permit flexing of the article without damaging of the piece.

In accordance with this invention the product of the process of this invention can be heat treated without the need of a protective atmosphere. In some instances the coating appears to turn dark but can be cleaned off by light brushing, etc. However no significant change in hardness of the case is found to occur as a result of the change in appearance.

Example 3

A number of drill rods fabricated from SAE 1090 steel (0.90% carbon) was coated by the process of this invention as outlined in Example 1 in a series of tests. The rod in a first test of the series was permitted to remain

in the bed and the bed to remain in the furnace until the entire mass had cooled to substantially room temperature. The result was that the core of the drill rod treated in this manner was annealed or normalized, i.e. the core is soft and flexible. The rod had a hard, relatively brittle case. However, the rod can be easily bent without substantial damage to the case. In a second series of tests, rods coated in accordance with the procedure set forth above were heated to a temperature of 1650° F. and were subjected to an oil quench. The result was that the cores were relatively brittle even though the cases had substantially the same characteristics as the case obtained by the previous heat treatment set forth in this example. Upon heating of the oil quenched articles to a temperature of 400° F. to 600° F. and air cooling the articles, the cores were converted to a condition of flexible toughness and the cases remained unaffected.

The examples set forth in numbered Examples 2 and 3 above are provided to illustrate that the articles produced in accordance with this invention do not require special atmospheric protection during the coating step, nor during heat treatment of the coated articles for the purpose of altering the characteristics of the core. The conventional heat treatment procedures have virtually no effect on the characteristics of the case produced in accordance with this invention.

Example 4

An article fabricated from steel having a carbon content less than 0.6% and having the shape of a cylinder was carburized in a conventional manner to alter the surface characteristics of the cylinder. An end of the cylinder was then sawed off to sever that end portion from the remainder of the cylinder. The end portion **30** thus had two ends, the carburized end having a high carbon content, and the cut end having a varying carbon content ranging from very high at the former outer and inner edges to below 0.6% in the median areas of the cut, exposed end. The outer and inner surfaces of the cylinder have a high carbon content. This article was treated in accordance with this invention under the procedure set forth in Example 1 above. The resulting coated article was found to have a uniformly high shiny polished appearance at the outer and inner circumferences of the cylinder and at the carburized end of the cylinder as viewed in FIG. 4. However the cut end was not uniformly coated. As viewed in FIG. 5, the region **31** adjacent the outer circumference of the cut end and the region 32 adjacent the inner circumference of the cut end had a highly lustrous hard uniform coating and the median region **33** which was originally the interior of the carburized article had virtually no coating deposited thereon as a result of the procedure of this example also illustrated the drop in ample is to illustrate the use of this invention on articles fabricated from relatively low carbon steels and which, without pre-carburization, are not coated in accordance with this invention. However they can be coated in accordance with this invention after having been surface treated by carburizing or other conventional processes to raise the carbon level at the surface thereof. Incidentally the procedure of this example also illustrated the drop in carbon content of the cut cross section of the cylinder with increasing depth, as reflected by the gradient from highly lustrous uniform coating in the region of shallow depths gradually diminishing in uniformity and quality as the depths increased until the innermost region 33 showed virtually no coating and a rather corroded general appearance.

Example 5

A sheet of copper was imprinted with a colloidal carbon suspension in kersosene ("DAG"), and the carbon imprint was permitted to dry. The sheet of copper was treated in accordance with this invention under the procedures outlined in Example 1 above after which the copper sheet was found to have a shiny white imprint conforming exactly to the carbon imprint. The shiny white imprint was found to be extremely hard carbide material which resisted etching action of conventional copper etching solutions.

Example 6

The procedure of Example 5 was repeated except that the carbon imprint was made on a ceramic article. The result was that the ceramic article had incorporated therein a white shiny hard metallic appearing imprint conforming exactly to the carbon imprint previously imparted thereto.

Example 7

A graphite crucible was treated in accordance with the procedures set forth in Example 1 above, except that a four hour period at operating temperature was employed. The result was thatt he crucible had a highly dense, metallic-appearing layer at the entire surface thereof this layer being highly resistant to the action of chemicals.

Example 8

Conventional burnishing balls were treated in accordance with the procedure set forth in Example 1. However, in order to avoid any possibility of contact between burnishing balls while they were imbedded in the bed of this invention, the individual balls were wetted with oil and then rolled in the powder used to make up the bed. The individual balls were thus covered with a layer of the bed powder which automatically separated the balls from one another when they were placed in the bed. After treatment in accordance with the procedure set forth in Example 1 it was found that the coating imparted thereto was an extremely hard, shiny, coating having a polished lustrous appearance and having a thickness of .0005". Thus the procedure of this invention is an excellent convenient technique for modifying the diameter of articles such as burnishing balls in a controlled fashion to achieve small uniform increase in the dimensions thereof.

Example 9

Ball-bearings made of 52100 steel were treated in accordance with the procedure set forth in numbered Example 8. The resulting coated ball-bearings were found to have an extremely hard surface having a smooth polished metal appearance. Ball-bearings coated in accordance with this procedure were placed next to otherwise identical untreated ball-bearings on a smooth inclined plane. Both sets of balls were released simultaneously and due to the improved surface characteristics the balls treated in accordance with this invention reached the bottom of the inclined plane ahead of the untreated ball-bearings.

Example 10

Steel rods of 1090 steel (0.90% carbon) were imbedded in a bed in a tube as described in Example 1 above, except that the rods were sufficiently elongated to pass through both portions, i.e. through the heated and unheated portions of the bed, and to extend into the atmosphere above the bed. A sensitive device for detection of electrical potential was connected to the rods and to the Inconel tube confining the bed. At room temperature no electrical potential was observed. As the heating progressed to about 400° F. definite polarity was observed, the tube being negative and the parts imbedded in the bed being positive. This polarity prevailed until the temperature of about 1700° F. was encountered and within a very small temperature range at 1700° F. the polarity was observed to reverse. Thus at temperatures above 1700° F. the part within the bed showed a negative polarity and the Inconel tube confining the bed showed a positive polarity.

In a separate experiment the procedures outlined immediately above in this numbered example was repeated except that two rods were imbedded in the bed and were connected to the positive and negative terminals, respec-

tively, of a 6-volt storage battery. After two hours at operating temperatures, and cooling to room temperature, the rod attached to the negative electrode was found to be vastly superior with respect to coating quality to the rod attached to the positive electrode.

Example 11

The procedure of Example 1 was repeated except that the bed was made up of the following ingredients: alundum (16.5%), ferrochrome (16.5%), chromium chloride ($CrCl_3$) (8.2%), barium chloride (58.8%). The results obtained in this example were substantially the same as the results obtained in Example 1 with respect to a coating quality. However it was observed that there was a more severe temperature lag on the interior of the bed presumably due to the fact that there was a substantially lower level of metal-source ingredients present in the bed of this numbered example.

Example 12

The procedure of Example 1 was again repeated except that the bed was made up of the following ingredients: Alundum (16.5%), ferrochrome (66.6%), chromium chloride ($CrCl_3$) (8.4%), barium chloride (8.5%). The results obtained in this numbered example were substantially the same as those obtained in Example 1 and reported in Table I therein. However, it was observed that the temperature lag of this numbered example was considerably less than the temperature lag in the bed of Example 1. I believe this is due to the presence of the extremely high level of metal-source component in the bed of this numbered example.

Example 13

The procedure of Example 1 was again repeated using the ingredients listed in Example 1 except that 10% sodium chloride based on the weight of the barium chloride was added to the ingredients. In small preliminary tests it was found that the addition of the 10% sodium chloride to the barium chloride lowered the temperature of insipient fusion with the result that the contact temperatures above 1500° F. could be employed. Thus in this numbered example the furnace was set to provide a maximum of bed temperature of approximately 1575° F. and the bed was maintained at that maximum temperature for approximately 2 hours. The results obtained in accordance with this numbered example were substantially the same as the results reported for Example 1 above.

Example 14

The procedure of Example 1 was again repeated using the ingredients as set forth in Example 1 except that the maximum bed temperature was limited to 1700° F. The bed was maintained at maximum temperature for approximately 2 hours. After the bed and its contents had cooled to room temperature the tube was emptied. It was observed that substantially no plug had formed within the bed and that the degree of coating on all of the articles treated in accordance with this example was entirely inadequate. In a separate experiment this procedure was repeated except that a maximum temperature of 2150° F. was utilized as the maximum bed temperature. It was observed however that the heated portion of the bed fused into an integral mass and was not suitable for immediate reuse in accordance with this invention.

I have observed that the maximum depth of the layer formed by the method of this invention is approximately .0005 inch in thickness. Thus the maintaining of the article in the bed at operating temperature beyond 2 hours does not provide a substantial increase in the thickness of the coating. However the maintaining of the bed for times substantially greater than 2 hours does lead to a change in the density of the coating. Thus when extremely dense surfaces are required, e.g. surfaces on a crucible it is preferred that longer periods of time be utilized, e.g. 4 hours.

However, on surfaces intended to carry lubricants it is preferred that shorter periods of time, e.g. less than 2 hours be employed, and that steels such as 1060 steel (0.6% carbon) be used. These steels are usually not uniform with respect to carbon distribution at the surface, the surface exhibiting both high carbon areas and low carbon areas. The use of such steels in accordance with this invention leads to a relatively uneven surface, microscopically speaking, there being a high degree of coating at the high carbon areas and a lower degree of coating at the lower carbon areas. Nonetheless, the overall appearance is that of a relatively polished metal. It is my belief that the microscopic unevenness is highly advantageous insofar as the surface is permitted to carry greater quantities of lubricant. Thus, in the coating of articles such as sealing rings, e.g. piston rings, I prefer to use rings fabricated from 1060 steel (0.6% carbon) and coat in accordance with the invention under conditions which provide a slight microscopic mottling effect. Using the mix described in numbered Example 1 above, the preferred contact time at operating temperatures is about 3 hours for the coating of articles such as piston rings.

Another advantage which results from the fact that the coating applied in accordance with this invention can be an extremely uniform coating is the fact that these coatings lead to virtually no change in the surface configuration of the article being coated. Thus irregularly shaped articles such as files, saw blades, drills, taps, surgical knives and the like, can be coated in accordance with this invention with the result that an extremely hard, abrasion resistant layer is formed thereon without significant alteration in the surface characteristics of the article. No edge buildup is observed as is common in chromium plating.

Balls and seats (1" diameter ball—52100 steel—1.00% carbon) designed for use in an oil well pump were coated in accordance with this invention. They had a useful life more than three times longer than the identical uncoated components when subjected to actual use in field conditions.

Articles coated to increase wear usually need no special treatment to re-distribute carbon to harden and "back-up" the micro-region immediately below the coating of this invention. Thus ejection pins designed for use in a plastic extruder needed no further treatment. However, I would prefer to increase carbon "back-up" of articles coated in accordance with this invention, if the article is to be used under high impact conditions. Thus I prefer to hold dental drills coated in accordance with this invention at 1600° F. for one hour as a post-treatment to permit migration of carbon from the interior of the article to the region under the coating. This hardness "backs-up" the coating making it even more suitable for high impact use.

While a special atmosphere is not necessary when heat treating articles coated in accordance with this invention, I prefer to protect articles which are treated at extremely high temperature, such as high speed tool steel (i.e. tungsten type) articles which (after coating) are hardened by quenching from about 2000° F.

As used herein, the term "halide" of chromium is intended to include, among the other halides, chromic chloride and chromous chloride and mixtures thereof. I have found that when hydrated chromic chloride is used as the halide bed ingredient, chromous chloride is present in substantial quantities in the bed after the first hearing cycle. I prefer, however, $CrCl_3 \cdot xH_2O$ as a bed ingredient, because it is readily available commercially, and has proven eminently satisfactory as an ingredient.

I claim:

1. The method of applying a carbide coating to a

surface of an article having 0.5% or more carbon, including the steps:

(1) Imbedding said article in a powder bed comprising the mixture

(a) 5% to 70% by weight of a first powdered ingredient selected from the group alundum, clay, firebrick, ceramics, said first ingredient being selected from materials which do not become tacky at temperatures encountered in this method,

(b) 5% to 90% of a second powdered ingredient selected from the group ferrochrome, chromium, ferromolybdenum, molybdenum, ferrotitanium, titanium, ferrotantalum-columbium, ferrocolumbian, ferrotungsten, tungsten, and mixtures thereof,

(c) 5% to 70% of a halide salt of the nonferrous metal selected as the third ingredient, and

(d) 7% to 80% barium chloride,

said powder bed being in pneumatic communication with the atmosphere and being in the first portion of a vessel having a first and second portion, the first portion being in direct pneumatic communication with the second portion, the second portion separating the first portion from the atmosphere;

(2) heating the portion of the vessel and the bed to a temperature of insipient fusion of the bed;

(3) maintaining the second portion at a lower temperature at which condensible volatiles moving from the heated first portion are condensed, and are thereby prevented from being moved into the atmosphere; and

(4) maintaining the article in the heated first portion for a period of time sufficient to deposit the required thickness of carbide deposits thereon.

2. A method of applying a chromium carbide coating to a surface of an article having 0.5% or more carbon, including the steps:

(1) imbedding said article in a first portion of a powder bed comprising the mixture

(a) 5% to 80% of a first powdered ingredient selected from the group alundum, clay, firebrick, ceramics, said first ingredient being selected from materials which do not become tacky at temperatures encountered in this method,

(b) 5% to 70% of a second powdered ingredient selected from the group ferrochrome, and chromium, and mixtures thereof,

(c) 5% to 70% chromium chloride, and

(d) 7% to 80% barium chloride,

said powder bed being in pneumatic communication with the atmosphere and having a first portion and a second portion, the first portion being in direct pneumatic communication with the second portion, the second portion residing between the first portion and the atmosphere;

(2) heating the first portion of the bed to a temperature of inspient fusion of the bed;

(3) maintaining the second portion at a lower temperature at which condensible volatiles moving from the heated first portion are condensed therein, and are thereby prevented from being moved into the atmosphere; and

(4) maintaining the article in the heated first portion for a sufficient period of time for a deposit of the desired thickness to form thereon.

3. The method of claim 2 in which the bed comprises the mixture including: alundum in an amount between 5% and 50% inclusive; a member selected from the group ferrochromium and chromium, in an amount between 5% and 50% inclusive; chromium chloride ($CrCl_3$), in an amount between 7% and 30% inclusive, and barium chloride in an amount between 10% and 80% inclusive, all amounts being expressed in precent by weight of the weight of the bed.

4. The method of claim 3 in which the first portion of the bed is heated to a temperature between 1800° and 2000° F. inclusive.

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