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[54] **DIFFUSION COATING OF FERROUS ARTICLES**
15 Claims, No Drawings

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ABSTRACT: Improved diffusion coatings on ferrous articles are achieved using pack diffusion techniques when both a source of silicon and boron are present in the pack composition. The silicon comprises from about 1 percent to about 7 percent by weight of the pack composition, and the boron comprises from about 0.5 percent to about 4 percent by weight of the pack composition. Diffusion coatings having a thickness on the order of 30 mils and greater are obtained.

DIFFUSION COATING OF FERROUS ARTICLES

BACKGROUND OF THE INVENTION

This invention relates to the diffusion coating of ferrous metal articles.

In the production of ferrous metal tools and parts, it is often desirable to provide a wear-resistant surface thereon to substantially increase the life of the article. An example of such a tool is a muller blade, the surfaces of which are subject to substantial wear. Without special treatment, muller blades made of mild steel would rapidly wear and would have to be replaced at frequent intervals. However, by proper surface treatment, a hard, wear-resistant surface can be provided on the muller blade which improves its performance and increases the useful life of the blade. In other cases it may be desirable to have a corrosion resistant or heat-resistant surface on the article, depending upon the environment on which the article is to be used. As an example of such a use would be impeller blades and other parts for use in gas turbines, furnaces and the like.

A particularly useful method for providing improved surfaces on ferrous metal articles is known as dry pack diffusion. By this method, the surfaces of ferrous metal articles are treated by diffusing a metal such as chromium, titanium, or tantalum into the surface area of the metal article being treated, thereby to form on and within the surface area of the article a diffused coating or layer having substantially improved physical and chemical characteristics over the base metal.

As is understood, dry pack diffusion is carried out by imbedding the metal article to be coated in a dry impregnating pack comprising a mass of filler material, a source of metal or metals to be diffused into the surface of the article and a source of halide which volatilizes at diffusion temperatures, as a carrier for the diffusion coating process. The pack is sealed and heated to a temperature on the order of about 1,300° F to about 2,100° F. in a reducing atmosphere for a sufficient period of time, so that the halide is volatilized and combines with the pack metal to form a metal halide which diffuses into the surface of the article being treated. The diffused metal halide is reduced to the metal which forms, in the surface area of the ferrous metal article, an intermetallic coating or layer comprising the diffused metal and iron, said coating or layer having improved physical and chemical characteristics. As used herein the terms "coating" and "layer" are used interchangeably and refer to the area at and adjacent the surface of a treated article wherein the diffused intermetallic composition formed in the course of pack diffusion coating processes is situated.

Articles treated according to conventional prior art diffusion coating methods are generally characterized by having only relatively thin diffusion coatings thereon, on the order of only a few mils, which coatings can be rapidly worn away during use of the article, thereby requiring frequent replacement and recoating.

In addition, it has been found that the carbon content of the article being treated by conventional methods has a deleterious effect on the coating process. It has been observed, for example when coating steel having a carbon content of about 0.3 percent that a carbon barrier is formed by the carbon of the article adjacent the surface of the article during the diffusion coating process, which barrier apparently inhibits the diffusion coating process and the resulting coating is substantially thinner than coatings obtained on lower carbon steels treated under the same conditions.

SUMMARY OF THE INVENTION

It has been discovered that thick diffusion coatings comprising metal selected from groups IV(*b*), V(*b*) and VI(*b*) of the periodic chart of the elements can be applied to the surface of ferrous metal articles regardless of the carbon content of the article by pack diffusion methods when both a source of silicon and a source of boron are present in the pack composition. In accordance with this invention, diffused coatings as thick as 30 mils and greater have been obtained which heretobefore were not obtained by the use of conventional pack diffusion methods.

In carrying out the method of this invention, the impregnating pack comprises a source of silicon and a source of boron, a halide which is volatilized at pack diffusion temperatures, a metal which is to be diffused into the surface of the ferrous article and a filler material. As mentioned above, the metals used for forming the diffusion coatings are selected from groups IV(*b*), V(*b*) and VI(*b*) of the periodic chart of the elements. These elements include chromium, titanium, tungsten, tantalum, vanadium, zirconium, hafnium, niobium and molybdenum. These metals have the properties of forming tough, wear-resistant diffused intermetallic coatings in the surface area of ferrous metal articles. The metal comprises from about t2 to about 35 percent by weight of the pack composition.

The halide component of the pack composition constitutes from about 0.1 to about 6 percent by weight of the pack composition. The preferred halide source is an ammonium halide such as for example, ammonium chloride and ammonium iodide, since it provides both the halide and reducing agent. However, any halide source which is vaporized at coating temperatures can be used in this invention, such as for example, the hydrogen halides, which also provide the reducing atmosphere, or halides in combination with a reducing atmosphere such as hydrogen.

As a source of silicon in the pack composition of the invention, silicon metal is highly preferred. The silicon source normally has a particle size from −80 to +325 mesh. Although particle size of the silicon source is not considered critical, it has been found that more uniform diffusion coatings are achieved when the components of the pack are finely divided and thus it is preferred that the particle size of the silicon source be 120 mesh or finer.

The silicon content of the pack should comprise at least about 1 percent by weight of the pack. Best results have been obtained when the silicon content of the pack is between about 1 to about 7 percent by weight of the pack.

In addition to silicon metal, other silicon containing materials which, at pack diffusion temperatures provide free silicon, can be used as a source of silicon. A prime example of such a material is silicon carbide. At the diffusion coating temperatures employed sufficient free silicon is obtained from the silicon carbide to provide the silicon required to obtain the improved diffusion coatings in accordance with this invention.

Boron metal is the preferred source of boron in the pack composition of this invention. The boron metal is used in highly divided or powdered form which is available commercially. Boron comprises at least about 0.5 percent by weight of the pack composition, and best results have been achieved when the boron content of the pack comprises from about 0.5 to about 4 percent by weight of pack. In addition to boron metal, other boron containing materials which provide free boron at pack diffusion temperatures, such as for example, boron carbide can be used.

The remainder of the pack composition consists of filler material. A highly preferred filler material is aluminum oxide. Aluminum oxide is preferred because it has the property of forming, when used in accordance with this invention, an additional abrasion resistant coating over the diffused coating on the surface of the ferrous metal article. This coating comprises aluminum oxide particles bound by a matrix of the diffusion coating metal and iron.

In addition to alumina, other refractory materials, such as magnesium oxide, sand, silicon carbide and boron carbide are useful as filler materials for the pack compositions of this invention. As pointed about above, both boron carbide and silicon carbide can be used as the boron and silicon source as well as the filler material for the pack compositions of this invention.

The following example illustrates a preferred method for forming improved surfaces on ferrous metal articles in accordance with this invention.

EXAMPLE 1

Samples of various carbon steels were selected for pack diffusion coating chromium onto the surface thereof. Steel samples consisted of SAE 1010 (about 0.1% C), 1020 (about 0.2% C) and 1030 (about 0.3% C) steel. Two samples of each type of steel were placed in four inconel retorts labeled (A), (B), (C) and (D), respectively. The samples in each of the retorts were surrounded by and imbedded in a pack composition in accordance with standard pack diffusion techniques. The composition of the packs in each of the retorts was varied as set forth below:

Pack Composition Percent by Weight

	A	B	C	D
Boron	0	2	0	2
Silicon	0	0	4	4
Chromium	20	20	20	20
Aluminum Oxide	77	75	73	71
Ammonium Chloride	3	3	3	3
	100	100	100	100

Each of the retorts was sealed with a glass seal and placed in a suitable furnace and maintained therein for 6 hours at a temperatures of 2,050° F. At the completion of the run, the retorts were removed from the furnace and the samples were removed therefrom for petrographic inspection. It was noted in cutting up the samples for examination, that the samples from retort D were extremely hard to cut, requiring approximately five times as much time on the cut off wheel as for the other samples. Upon petrographic inspection it was noted that each of the steel samples from retorts A, B and C had relatively thin diffused coatings on the order of about 0.5 for the SAE 1030 steel to about 3.5 mils for the SAE 1010 steel, while the samples from retort D had a diffusion coating on the order of 30 mils. In addition, it was noted that the samples from retort D had an outer coating over the diffusion coating which consisted essentially of particles of aluminum oxide bonded by a matrix comprising chromium and iron in indeterminate proportions with traces of silicon and boron.

The following example illustrates another embodiment of this invention, wherein silicon carbide was substituted for aluminum oxide as a filler material in the pack composition.

EXAMPLE 2

One sample each of SAE 1010, 1020 and 1030 carbon steel was placed in an inconel retort for pack diffusion coating in the manner set forth in example 1 above. The pack composition consisted of 3 percent ammonium chloride, 2 percent boron metal, 4 percent silicon metal, 20 percent chromium metal and 71 percent silicon carbide. The retort was sealed and placed in a furnace where it was maintained at a temperature of 2050° F. for 6 hours. At the completion of the 6-hour period, the retort was removed from the furnace, cooled, opened and the samples removed and cut cut for petrographic inspection. Each of the samples had a diffused coating of between 60 to 80 mils in thickness. No outer coating of silicon carbide could be observed.

EXAMPLES 3–12

The following examples illustrate some other pack compositions which have been used in accordance with this invention to form thick diffusion coatings on ferrous metal articles.

PACK COMPOSITION, PERCENT BY WEIGHT

	Example									
	3	4	5	6	7	8	9	10	11	12
W								10.0		
Cr									20.0	20.0
Ta					4.1		4.1			
Ti						4.1	4.1			
NH_4Cl	0.5	0.3	1.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
Si	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
B	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	
Al_2O_3	93.5	93.7	93.0	91.0	86.9	86.9	82.8	81.0		
B_4C									71.0	73.0

By the use of both a source of silicon and a source of boron in the pack composition in accordance with this invention improved diffused coatings have been applied to a variety of ferrous metal alloys ranging from steels very low in carbon content, on the order of 0.001 to 0.003 percent, up through SAE 1010, 1020 and 1030 steels all the way to grey cast iron and nodular cast iron. In addition, the pack compositions of this invention have been used successfully on various stainless steels and special alloy steels. The diffused coatings obtained are ductile, tough, wear-resistant and strongly adhering to the base metal. The thickness and hardness of the coating can be controlled by varying the time and the temperature at which the article being treated is subjected to diffusion coating in accordance with known pack diffusion techniques. The times and temperatures are not critical except as broadly set forth above and those skilled in the art can readily determine the optimum time and temperature for coating articles in accordance with this invention.

While the invention has been described in connection with specific embodiments thereof, it will be understood that it is capable of further modification, and this application is intended to cover any variations, uses or adaptations of the invention. It will, therefore, by recognized that the invention is not to be considered limited to precise embodiments shown and described, but is to be interpreted as broadly as permitted by the appended claims.

I claim:

1. A method particularly adapted for providing a deep protective surface, on the order of 30 mils, for ferrous articles by dry pack diffusion treatment, comprising the steps of imbedding said article in a diffusion coating pack composition comprising on a weight percent basis 2–35 percent of a metal selected from the group consisting of the metals of groups IV(*b*), V(*b*) and VI(*b*) of the periodic chart of the elements and combinations thereof, a source of silicon, the silicon content thereof comprising at least about 1 percent of said pack, a source of boron, the boron content thereof comprising at least about 0.5 percent of said pack, and from about 0.1 to about 6 percent of a vaporizable halide, heating said pack composition while said article is imbedded therein to effect the vaporazation of said halogen and diffusion of said metal into the surface of said article.

2. The method of claim 1 wherein said silicon comprises from about 1 to about 7 percent by weight of said pack and said boron comprises from about 0.5 to about 4 percent by weight of said pack.

3. The method of claim 2 wherein said silicon comprises 4 percent by weight of said pack and said boron comprises 2 percent by weight of said pack.

4. The method of claim 1 wherein said source of silicon is silicon metal.

5. The method of claim 1 wherein said source of silicon is silicon carbide.

6. The method of claim 1 wherein said source of boron is boron metal.

7. The method claim 1 wherein said source of boron is boron carbide.

8. The method of claim 1 wherein said source of vaporizable halide is an ammonium halide.

9. The method of claim 8 wherein said ammonium halide is ammonium chloride.

10. The method of claim 8 wherein said ammonium halide is ammonium iodide.

11. The method of claim 1 wherein said source of metal for said diffusion is chromium.

12. The method of claim 1 wherein said source of metal for said diffusion is tantalum.

13. The method of claim 1 wherein said source of metal for said diffusion is titanium.

14. The method of claim 1 wherein said source of metal for said diffusion is titanium and tantalum.

15. The method of claim 1 wherein said pack composition and said base imbedded therein are heated to a temperature of between about 1,300° F. to about 2,100° F. thereby to effect diffusion of said metal.

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