

[72] Inventor **Howard D. Flicker**
 North Miami, Fla.
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 [73] Assignee **API Corporation**
 Miami, Fla.
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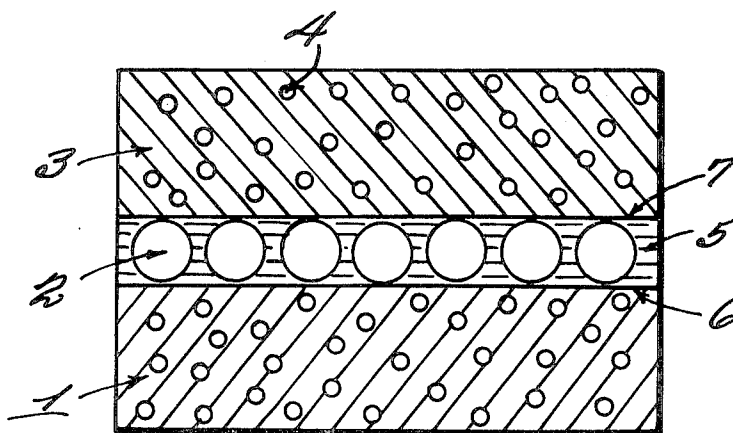
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Primary Examiner—Alfred L. Leavitt
Assistant Examiner—C. K. Weiffenbach
Attorney—Cushman, Darby & Cushman

[54] **DIFFUSION COATING**
 6 Claims, 1 Drawing Fig.

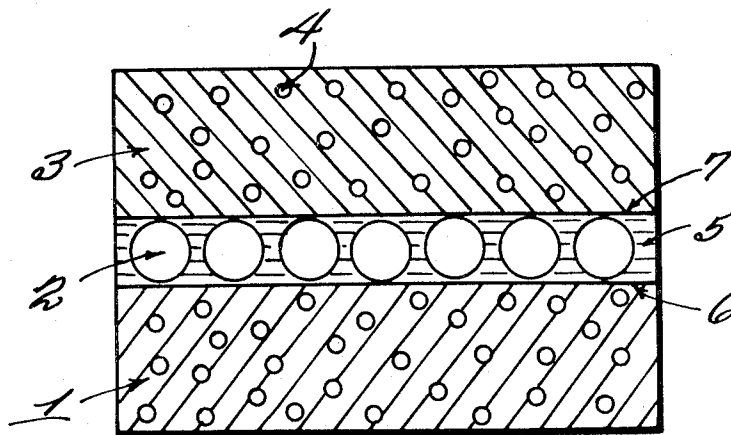
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ABSTRACT: There is provided a surfaced alloyed metal product and a method for production thereof. The metal part to be surface alloyed is coated with a decomposable compound, coated with an alloying material, and heated to an elevated temperature above the decomposition temperature of the decomposable compound in a dry gaseous atmosphere, especially in a hydrogen atmosphere. The decomposable compound must contain at least one element which has an atomic volume greater than the atomic volumes of the elements of the metal part to be surface alloyed and the alloying materials. Preferably the decomposable compound contains an element which has an atomic volume at least 1.1 times the atomic volumes of the metal part and alloying material.



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INVENTOR

HOWARD D. FLICKER

BY

Cushman, Darby & Cushman
ATTORNEYS

DIFFUSION COATING

This application is a continuation-in-part of application Ser. No. 635,476, filed May 2, 1967, now U.S. Pat. No. 3,535,146.

This invention relates to novel surfaced alloyed metal articles or substrates and to a method for production thereof.

It is known in the art to form surfaced alloyed metal articles by techniques generally referred to as diffusion alloying or diffusion coating. Heretofore, such articles were produced by a number of methods such as: a vacuum chamber or sputtering technique to coat the metal article with a second metal composite and heating to cause diffusion and alloying; plating the metal article with a second metal and thereafter heating to cause diffusion and alloying; packing a metal powder around the metal article and heating to cause diffusion and alloying.

While all of the above-mentioned techniques provided useful products, the articles so produced suffer from common disadvantages. When such surface alloyed products are subjected in service at high temperatures, such as the temperature commonly encountered in jet engines, the alloying metals or compound contained in the coating begin to further diffuse into the metal part whereby the composition of the alloyed surface begins to radically change. If exposed for extended periods of time or for short periods of time at very high temperatures, this diffusion will diminish the amount and proportions of the alloying metals of the surface of the part to a point where the useful properties of the alloyed surface no longer exists and the part becomes unserviceable or, even worse, fails in use. Furthermore, the diffused coating thicknesses are difficult, if not impossible to control. Each process has limiting factors, for instance, because of the high vapor pressure, chromium cannot readily be diffused in vacuum. Aluminum cannot be diffused in atmospheres containing nitrogen, etc. Thus, two of the elements which are among the best for oxidation resistance can only be diffused with limited techniques.

It is, therefore, an object of this invention to provide a surface coated or alloyed metal article which will be substantially resistant to further diffusion at elevated temperatures. Another object is to provide a process for producing a surface coated or alloyed part which is simple in operation, inexpensive and will produce a surface coated alloyed part that is substantially resistant to further diffusion at elevated temperatures. Other objects will be apparent from the following disclosure and claims.

Briefly stated, the above objectives are accomplished by applying a coating on the metal substrate of at least one decomposable compound, applying a coating over the said decomposable compound of at least one alloying material, and subjecting the so coated metal substrate to an elevated temperature above the decomposition temperature of the said decomposable compound in a dry atmosphere, wherein the said decomposable compound contains at least one element which has an atomic volume greater than the atomic volumes of the elements of the said metal substrate and the said alloying materials.

The decomposable compounds must contain elements which have relatively large atomic volumes as compared to the atomic volumes of the substrate and alloying materials; preferably the atomic volume should be at least 1.1 times greater, as explained in greater detail hereafter.

The decomposable compounds must be chosen so that the decomposition temperature thereof is lower than the solidus (melting-freezing) temperature of the substrate metal, and it is preferable that the decomposition temperature should be at least 50° F. lower than the solidus temperature of the substrate material. However to avoid decomposition prematurely, the decomposition temperature should not be more than 1,100° F. lower than the solidus temperature of the substrate. However, the decomposition temperature should be at least 350° F.

As mentioned above, the decomposable compounds must contain elements having large atomic volumes compared to the atomic volumes of the substrate and alloying materials. There are many compounds which will satisfy the above requirements. The applicable compound of course depends upon the substrate and alloy-coating member. With a standard

chemical reference book such as Chemical Rubber Handbook, compounds which decompose at suitable temperatures with respect to the solidus temperature of the substrate can be determined and from these compounds can be selected those having an element with a larger atomic volume than either the substrate material or alloy-coating material. A partial listing of elements and their atomic volumes is included in the detailed discussion of the function of the barrier layer hereinafter.

The decomposable compounds are conveniently applied to the substrate with a lacquer made of any of the known organic film-forming materials which will be substantially burned away (noncarbonizing) at the elevated temperature utilized in the alloying step. While a host of such film-forming materials is known to the art, typical examples include polyvinyl chlorides, acetates and alcohols, polyesters, epoxies, nitrocellulose, polyolefins, natural and synthetic rubbers such as butadienestyrene, butyl, and neoprene, drying oils such as linseed, perilla and tung oils, and polyurethanes. The lacquer performs the function of holding the decomposable compounds in place while the temperature of the substrate is being raised. However, where the decomposable compounds decompose at relatively low temperatures, care must be exercised in choosing the particular lacquer since it is necessary that the lacquer be substantially burned away (noncarbonizing). Of course, a suitable solvent for the film-forming material will be necessary to prepare the lacquer and the amount of solvent will vary with the particular film former and the viscosity of the solution desired. It has been found that a particularly good lacquer may be prepared by dissolving pyroxylin in Cellosolve (ethylene glycol monoethyl ether, manufactured by the Union Carbide Corp.), in a ratio of about 3:100 to 20:100 by weight.

While the alloying materials may be in any soluble form with regards to a particular solvent, it is most convenient to use water soluble compounds such as salts or oxides of the alloying elements. Advantageously, small amounts of matrix-forming agents are added to the solution such as, one-fortieth to 2 percent of a soluble alginate. Preferably, the solution of the alloying materials is made by dissolving the materials in an aqueous solution of a silicate or borate that has been neutralized with a mineral acid such as hydrochloric, sulfuric or nitric acid. Suitable silicates or borates include the organic esters of acids such as ethyl and methyl silicates and borates, ammonium silicates, and the alkali metal silicates and borates such as sodium silicate. The silicates and borates are especially valuable since these not only form a matrix for holding the alloying metals but also have the property of adding a small silicon and/or boron component to the diffusion coating. Silicon and boron generally possess the property of creating an eutectic with other metallic elements. The amount of silicate or borate may be up to 15 percent dependent on the amount of silicon or boron desired in the diffused coat.

While it is preferable to use a saturated solution of the alloying materials, this is not necessary, and any proportion of alloying materials may be used. The particular ratio of the various alloying materials depends on the ultimate proportion of alloying elements desired in the surface-alloyed substrate. According to the invention, a wide variety of materials may be surface alloyed into a metal substrate and include chromium, aluminum, iron, zirconium, hafnium, silicon, nickel, titanium, tungsten, molybdenum, yttrium, columbium, cobalt, palladium, selenium, gold, vanadium and manganese. The above-mentioned materials are not all inclusive and are intended merely to illustrate the wide application of the present invention.

The temperatures used for drying the lacquer containing the decomposable compound and the coating containing the solution of alloying materials will depend on the particular lacquer and coating composition. Generally speaking, moderate temperatures are quite sufficient and fall within the range of room temperature to 500° F. The time of drying will depend on the temperature, speed of air currents over the coating, humidity and thickness of substrate but will generally be between 2 and

20 minutes. Of course, other temperatures and times may be used if desired. For example, when pyroxylin dissolved in Cellosolve is used as the lacquer, 140° F. is a satisfactory temperature. And when the solution of the alloying metals contains aqueous sodium silicate, 200° to 400° F. is a suitable drying temperature range.

The temperature to which the substrate is subjected after having been lacquered and coated will vary with the particular substrate. However, the particular temperature chosen, as noted above, must be above the decomposition temperature of the decomposable compound and it should be no more than 1,100° F. below the solidus temperature of the substrate. However, the decomposition temperature should be at least 350° F.

The length of time necessary to cause diffusion and surface alloying will of course depend on the substrate, alloying metals and decomposable compounds used, as well as the size of the part being surface alloyed and the degree of diffusion desired. Generally speaking, however, from 1 minute to 4 hours will be sufficient.

As a further feature of the invention, it has been found that superior products result when the alloying step is carried out in an atmosphere of dry gases such as dry hydrogen, cracked ammonia, endothermic and exothermic generated gas, and even dry steam, but not limited to these. Furthermore, it is especially advantageous when a reducing atmosphere is used, as the alloyed surface is more dense and more completely attached to the metal substrate. Also, a very important feature of the invention is the use of dry hydrogen as the reducing atmosphere, as such an atmosphere renders many compounds decomposable which would not decompose in air and also reduces the decomposition temperature of many of the decomposable compounds.

While the mechanism by which the present invention is accomplished is not completely understood, and while not being bound by theory, the following theoretical explanation will aid in understanding the invention, and in reference to the accompanying drawing wherein:

The FIGURE is a diagrammatic illustration of the product of the invention.

In the FIGURE, 1 is the substrate metal which may be any conventional metal or alloy such as, aluminum, stainless steel, nickel-base alloys, cobalt-base alloys, steel, copper, etc., 2 is the large atomic volume element of the decomposable compounds which have been decomposed. The alloying elements are denoted by 3 and 4, represents the individual atoms or molecules of the alloying elements. The diffusion zone (or zone of alloy) formed by the alloying materials diffusing toward the substrate and the substrate diffusing toward the alloying materials is denoted generally by 5. Hence, 5 is a solid solution of the alloying metals and the metal substrate. It is to be clearly understood that the lines of demarkations 6 and 7 between the alloying materials and the metal substrate are merely shown to explain the invention and are not intended to suggest that such clear lines actually exist. Actually, the alloyed surface is a solid solution with no distinct lines of demarkation between the alloyed surface and the substrate. Similarly, the relative thickness and distinction between the solid substrate 1 and the alloying metals 3 is not intended to be an actual depiction, but only to illustrate the invention. Of course the actual thickness of the alloyed coating may be as desired and is controlled in part by the thickness of the coating prior to diffusion and the extent diffusion is allowed to take place. The coating could be as little as 1 micron or as great as one-eighth inch.

When the substrate 1 has been coated with the lacquer containing the decomposable compound, dried, coated with the solution of alloying materials and dried, it is ready for subjecting to the elevated alloying temperature. As the temperature is raised to or past the decomposition temperature of the decomposable compounds, the compounds decompose and the elements become "nascent." The nascent elements are easily combined with any available atoms. Hence, for example, if the

large element of the decomposable compound is barium, the barium atoms will readily combine and firmly attach to or slightly diffuse in the metal substrate of, for example, steel. When a dry hydrogen atmosphere is used, the other element or elements of the decomposable compound, such as a sulfate radical when barium sulfate is used will combine with the hydrogen to form H₂SO₄ and readily vaporize off whereby the unneeded sulfate radicals are removed.

The large nascent atoms of the decomposable compound will attach to the metal substrate and will not substantially diffuse into the substrate. For example, if barium sulfate is the decomposable compound and iron is the substrate metal, the nascent barium atoms will attach to the iron atoms on decomposition of the barium sulfate, but will not substantially diffuse into the iron since the atomic volume of barium is 39 and iron is only 7.1. Therefore, the larger barium atoms will be substantially prevented from diffusing into the substrate of smaller iron atoms while the small iron atoms of the substrate, to a much larger extent, can diffuse into and through the barrier layer of barium atoms. Similarly, the smaller alloying atoms can diffuse through the barrier layer of barium atoms. It will be appreciated from the above, that only a one-atom-thick layer of the decomposable compound is necessary, but in practice this is almost impossible to achieve, and from a practical standpoint, the thickness of the layer may be as great as one-sixteenth inch or greater.

As a result of the above explained action, the objects of the invention are accomplished. Hence, when a metal article such as a jet engine part is surface alloyed according to the present invention, the barrier layer substantially reduces the amount of further diffusion of the alloying metals into the substrate at the temperatures encountered during use (which temperature of necessity must be safely below the solidus temperature of the substrate or alloyed surface).

From the above discussion, it will be apparent that the atoms making up the barrier layer must have a substantially larger atomic volume than either the substrate or the alloying metals. While some benefits can be obtained with barrier atoms only slightly larger than the alloying atoms and the substrate atoms, the barrier layer should preferably have an atomic volume of at least 1.1 times that of the alloying and substrate metal atoms and desirably more than 1.25 times larger atomic volume.

For many applications even better results are obtainable, since in many applications the barrier layer atomic volumes can be 2 times or greater that of the alloying and substrate atomic volumes, although as noted above good results are obtained with ratios of atomic volumes as low as 1.1. Table I below, which shows a number of common metals and alloying materials, illustrates the many possible combinations. Notice most of the common metals have an atomic volume of about 10 or less, while only a few have greater atomic volumes. Also notice that the last nine elements have atomic volumes of at least 20, most of which are from group IA and IIA of the periodic table. These elements would of course do very well as barrier layer atoms for the common metals and the alloying metals.

TABLE I

Elements	Atomic Volume, W/D
Iron	7.1
Cobalt	6.7
Beryllium	5.0
Magnesium	14.0
Yttrium	19.8
Lanthanum	22.5
Titanium	10.6
Zirconium	14.1
Hafnium	13.6
Vanadium	8.35
Chromium	7.23
Molybdenum	9.4

Tungsten	9.53
Manganese	7.39
Rhodium	8.3
Iridium	8.54
Nickel	6.6
Palladium	8.9
Platinum	9.1
Copper	7.1
Lead	18.3
Silver	10.3
Gold	10.2
Zinc	9.2
Cadmium	13.1
Aluminum	10.0
Silicon	12.1
Na	23.7
K	45.3
Rb	55.9
Cs	70
Ca	29.9
Sr	33.7
Ba	39
the	20.5
I	25.7

A very important feature of this invention is the great latitude it provides in choosing particular metal substrates, barrier layers and alloying materials, and, accordingly, is applicable to a wide variety of particular uses.

The following examples will serve to illustrate the invention, but the invention is limited only by the annexed claims.

COMPOSITION, PART BY WEIGHT

	Chromium	Nickel	Iron	Cobalt	Aluminum	Titanium	Columbium	Molybdenum	Manganese	Zirconium	Hafnium	Tungsten	Yttrium	Silicon
1	15.8	76.0	7.2											
2	15.6	79.5	.35		3.4	.7								.20
3	20.0	80.0												.20
4	13.0	(1)	1.0		6.0	.6	2.25	4.5						
5	22.0	(1)	18.5	1.5			.60	9.0						.50
6	27.0	2.5	2.0	(1)				5.5						1.0
7	26.0	3.5	(1)	.5										1.0
8	15.0	35.0	(1)						2.0					1.7
9	15.0	(1)	3.5	10.0		5.0		2.0		.5				1.0
10	20.0	20.0	.5	(1)	3.0	2.0		1.0		.5	.25	3.0	1.0	.5
11	25.0		70.0		4.0								1.0	

¹ Balance.

EXAMPLE 1

Two identical parts used in the combustion chamber of a jet engine were cleaned by brushing. The parts were made of Hastelloy X. A lacquer was prepared by dissolving 15 parts barium chromate in 50 parts of a 5 solution of pyroxylin in cellosolve. This lacquer was painted on the parts and dried at 140° F. for 10 minutes. An aqueous solution was prepared having the following composition by weight:

Cobalt Chloride 45%
Ammonium Silicate 5%
Water 50%

The aqueous solution was coated on the parts and dried at 240° F. for 10 minutes. The parts were then subjected to a temperature of 2,100° F. for 30 minutes in an atmosphere of dry hydrogen. After cooling the parts slowly to room temperature, the surface alloyed parts were vapor blasted.

One of the parts was stored at room temperature while the other part was subjected to 2,000° F. for 24 hours. The two parts were then identically sectioned and the part held at the elevated temperature was compared with the part held at room temperature. There was no evidence of further diffusion in the part held at the elevated temperature.

EXAMPLE 2

The procedure of example 1 was repeated in three additional tests, except that the barium chromate was replaced by the following decomposable salts in each test respectively, and the temperature to which the parts were subjected were as noted opposite the particular compounds:

Barium Chloride 10w/w% 2,000° F.

Calcium Chloride 10w/w% 2,000° F.

Potassium Chloride 10w/w% 2,000° F.

5 The results in each of the above tests showed that no further diffusion takes place in the part held at the elevated temperature.

EXAMPLE 3

10 Ten metals alloying solutions were prepared by dissolving various proportions of the following compounds in a 4 percent aqueous solution of ethyl silicate:

Chromium Chloride
Nickel Sulfate
Iron Oxide
Cobalt Chloride
Aluminum Chloride
Columbium Chloride
Molybdenum Disulfide
Manganous Sulfate
Zirconium Oxide
Hafnium Oxide
Tungsten Bromide
Yttrium Oxide
Ammonium Silicate

The solutions were saturated and had the following compositions of the metal ions by weight:

Jet engine parts made of each of the following metals were prepared for testing:

45 410 stainless steel
303 stainless steel
1010 steel
hastelloy X

50 The parts were cleaned and lacquered with a 5 percent solution of pyroxylin in cellosolve and containing 35 parts/hundred by weight of barium chromate as the decomposable compound. After drying at 180° F. for 10 minutes, one part made of each metal was coated with each of the metals alloying solution, dried at 240° F. for 10 minutes and subjected to a dry hydrogen atmosphere at 2,000° F. for 30 minutes. Each part was sectioned and the alloy-coating analyzed for the percent of each metal in the coating. The coatings were determined to have the same compositions as the metal alloying solutions noted in the table above.

EXAMPLE 4

65 The procedure of example 3 was repeated except the jet engine parts were made of Rene 41 and Inconel 702 using solutions 2, 4 and 10 but without the silicon in solutions 2 and 4. Upon inspection of the finished parts, a well-adhered alloyed coating was apparent.

EXAMPLE 5

75 The procedure of example 1 was repeated except aluminum was used as the metal of the engine parts and palladium chloride alloying agent in a 20 percent solution was coated thereon. The diffusion temperature was 1,000° F. The same results as in example 1 was found, e.g. no evidence of further diffusion.

In example 3 it was shown that such metals as molybdenum and manganese can be used as the alloying material. The versatility of the present invention is demonstrated by the following examples wherein molybdenum and manganese are utilized as the barrier layer component.

EXAMPLE 6

The procedure of example 1 was repeated, except that the barium chromate was replaced by the decomposable salt molybdenum oxide. The results of the elevated temperature tests showed that no further diffusion takes place in the part held at the elevated temperature.

EXAMPLE 7

The procedure of example 1 was repeated except that the barium chromate was replaced by the decomposable salt manganese sulfate and the substrate part was made of nickel. The results of the elevated temperature tests showed that the cobalt coating diffused only slightly more at elevated temperatures than the cobalt coating of example 1.

EXAMPLE 8

The procedure of example 1 was repeated except that the barium chromate was replaced by the decomposable salts of molybdenum oxide and manganese oxide in a weight ratio of 20:1, respectively and the substrate part was nickel. The results of elevated temperature tests showed that no further diffusion takes place in the part held at elevated temperature. This example illustrates that the decomposable compound may actually be a mixture of compound having barrier elements with the ranges of atomic volumes, as defined above.

EXAMPLE 9

The procedure of example 1 was repeated except that the decomposable compound was molybdenum oxide and manganese oxide in a weight ration of 20:1, respectively, the substrate was hastelloy X and the metal-alloying solution had the metal ions composition of 11) in the table of example 1. The results of elevated temperature tests showed that no future diffusion takes place in the part held at elevated temperature. This particular coating is a very superior coating since it withstands oxidation and sulfidation at temperatures above 2,200° F., and is, therefore a preferred coating. However, the coating composition may vary between the ranges of Chromium 12-30; Aluminum 3-12; Yttrium 0.5-4; balance Iron, all

proportions being in parts by weight.

Having described the invention, it is readily apparent to one skilled in the art that a number of modifications thereof may be made without departing from the spirit of the invention and such modifications are to be contemplated as embraced within the scope of the following claims.

What is claimed is:

1. A process for alloying a metal substrate with an alloying metal comprising:

1. applying a first coating on said metal substrate of at least one decomposable inorganic compound in a noncarbonizing film-forming material, said decomposable compound containing at least one element selected from the group consisting of Mn and Mo having a decomposable temperature of at least 350° F. and at least 50° below the solidus temperature of the metal substrate said element having an atomic volume at least 1.1 times the atomic volume of elements of the said metal substrate and alloying metal,

2. drying said coating on said substrate,

3. applying a second coating of an aqueous solution of at least one reduceable salt or oxide of an alloying metal,

4. drying said second coating,

5. subjecting the so-coated substrate in a dry, gaseous atmosphere to an elevated temperature sufficient to decompose said decomposable compound and thereby forming a barrier layer of said at least one large element of the said decomposable compound and to reduce said reduceable salt or oxide to an alloying metal capable of alloying with said metal substrate thereby forming a surface alloy coating, and whereby said large element of said barrier layer is disposed on or partially in the surface of said metal substrate and said alloying metal is disposed on and through said barrier layer.

2. The process according to claim 1 wherein the said coating of alloying metal is applied in an aqueous solution containing a member selected from the group consisting of organic borates and silicates and inorganic borates and silicates.

3. A process according to claim 1 wherein the said decomposable compound contains Mn.

4. A process according to claim 1 wherein the said decomposable compound contains Mo.

5. The process according to claim 1 wherein the said coating of alloying metal comprises Chromium, Aluminum, Yttrium and Iron.

6. The product produced by the process of claim 1.

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