

[54] **DIFFUSION COATED METALLIC SUBSTRATE**

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[58] **Field of Search**..... **117/130 R; 29/196.2, 29/196.4, 196, 194**

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[57]

ABSTRACT

A diffusion coated metallic substrate is formed by providing a coating metal or element and a balancing metal or element on the substrate and adjusting the amount of the coating and balancing elements or metals so that the resulting coating has a coefficient of thermal expansion approximately the same as the substrate. A large atomic volume element is included in the coating to fill void flaws in the coating.

7 Claims, No Drawings

DIFFUSION COATED METALLIC SUBSTRATE

The present invention relates to diffusion coatings and more particularly to diffusion coatings which will tightly adhere to the coated substrate and substantially reduce the tendency of such coatings to spall or otherwise deteriorate.

Diffusion coatings have been used in the art for coating metal parts with a protective coating which allows the metal parts to operate, especially at elevated temperatures, without disruptive oxidation, thermal shock, erosion and loss of strength characteristics. Many different coatings and coating techniques have been suggested by the art. Generally, the approach taken by the art has been that of diffusing a metal or metals into the part to be protected, which metal or metals have a greater resistance to corrosion, oxidation, thermal shock, etc. than the part to be protected. For examples of such prior art approaches and as background to the present invention see U. S. Pat. Nos. 2,900,276; 3,096,160; 3,205,090 and Re. No. 26,001, which patents are incorporated herein by reference and show coating compositions which are representative of these prior art approaches.

Such approaches have worked relatively well, except that failures in the coated part begin to appear with extended use thereof, especially at elevated temperatures. For example, jet engine parts, which are subjected to elevated temperatures, show spalling, cracking and deterioration of the coating with prolonged use.

Accordingly, it is an object of the present invention to provide a diffusion coating composition and a process for applying the composition to a metal part, whereby the coated metal part will exhibit an increased service life. Other objects will be apparent from the following disclosure and claims.

Basic to the present invention is the discovery that failure of coated metal parts after extended service, especially at elevated temperatures as encountered in jet engines, is in a large measure a result of improper physical balances in the coating and between the coating and the coated substrate. To illustrate the aforementioned imbalance, when a metal part has a coefficient of thermal expansion of X and the coating has a coefficient of thermal expansion of $X + Y$ (Y being a positive or negative number), upon thermal cycling, i.e. from a low temperature to a high temperature and vice versa, the coating and metal part will expand and contract to different ultimate dimensions, whereby strains are generated in the coating and metal part. For example, if a coating is applied to a jet engine part at some temperature, e.g. 1,200°F, the dimension of the coating and part will be the same at that temperature. If the jet engine part is operated in the working jet engine at 1,200°F, the dimensions will be compatible. However, when the engine is cooled (when not working) or if the engine part is operated above or below 1,200°F, the dimensions will not be compatible and strains will result. Cycling the temperature of the part causes successive generation of various strains, and the extended use of the parts with cyclic induced strains eventually results in spalling, cracking and deterioration of the coated part.

Another imbalance leading to failures is the imbalance of relative size of the atoms in the coating. For best balance in the coating, there should be both large and small atoms in order to assure that a well packed homogeneous crystal structure in the coating will exist.

Furthermore, void flaws in the parts cause discontinuities and uneven physical properties which can cause stress concentrations and failure of a coated part.

It is therefore an object to provide a coated metal part and a process for producing the same which substantially overcomes the above imbalances and significantly extends the useful life of the coated part. Other objects will be apparent from the following disclosure and claims.

Accordingly, in order to mitigate the imbalances above, the present coating comprises (1) a coating metal of relatively low melting temperature for diffusion coating of a metal part, (2) an element or metal which has a large atom size to fill void flaws in the coating and metal part, and (3) an element or metal having a coefficient of thermal expansion chosen so that the resulting coating has a coefficient of thermal expansion substantially the same as that of the metal part. With such a coating, void flaws are mitigated, a well packed crystal structure of the coating is obtained and the coated metal part has a balanced coefficient of thermal expansion.

The coating metal must have a relatively low melting temperature in order that it may be diffused into the metal part at a temperature below the melting temperature of the metal part. In this regard the melting point of the coating metal or element must be below the melting point of the substrate to be coated, e.g. 50°F and especially 100°F or 250°F below. Of course, it is preferred that the coating metal or element be relatively resistant to corrosion and higher temperatures, as is known in the art, such as aluminum, chromium, nickel, cobalt, silver, tin, etc. and alloys thereof. These coating metals and their alloys have various coefficients of thermal expansion. For example, aluminum, tin and silver have relatively high coefficients of thermal expansions, e.g. about 2.36×10^{-6} per °C for aluminum and most of the alloys thereof, while nickel and cobalt have medium range coefficients, e.g. 13.3 and 13.8×10^{-6} per °C, and chromium and silicon have relatively low coefficients, e.g. 6.2 and $2.8-7.3 \times 10^{-6}$ per °C. On the other hand, common substrates (parts to be coated) such as iron and common ferrous alloys have coefficients of thermal expansion of as low as 9×10^{-6} to about 15.0×10^{-6} per °C. Some of the common metals and elements are shown in Table I.

TABLE I

		Ave.* coefficient of thermal expansion $\times 10^{-6}$ per °C (1 SIGN. FIG.)
METAL OR ELEMENT		
	Silicon	3
	Tungsten	4
	Molybdenum	5
	Zirconium	5
	Chromium	6
	Tantalum	7
	Columbium	7
	Titanium	9
	Antimony	9
	Platinum	9
	Beryllium	12
	Cobalt	14
	Steels (SAE NO.)	
	1008	15
	1022	15
	1040	15
	1085	14
	30705	20
	30915	19
	51710	13
	Aluminum and Alloys	24
	Nickel and Alloys	13.3
	Magnesium	22

Manganese
Tin and Alloys
Silver

22
21-25
30

*Data is not precise but merely for illustration purposes

As can be seen from the Table, if, for example, a tin coating is placed on a steel substrate of SAE 51710, the coating would have a coefficient of thermal expansion much greater than the steel substrate and the above noted imbalance would result. However, if the tin is alloyed with, for example, silicon, the relative amounts of silicon and tin could be adjusted to give a coating which has substantially the same coefficient of thermal expansion (hereinafter referred to " α "). Obviously, however, there are some practical limitations on this balance, since if, for example, silver were balanced with platinum to correspond with the α of steel, the amount of platinum required would drastically change the resulting coating, as well as being quite expensive. Hence, it is necessary that the coating be balanced with a metal or element having an α which is significantly different from the α of the coating. Specifically, the ratio of the balancing metal or element α to the coating α should be at least 1:2 and preferably 1:3 or 1:4 or greater, e.g. 1:15. Of course, the visa versa, is also true, i.e. the ratio of the coating α and the balancing metal or element α should be within the same ranges. Also, the coating α should not be too different from the α of the substrate, such as a ratio of the α of the coating to an α of the substrate of less than 5:1, preferably 4:1 and especially 3:1, e.g. 2:1 or less. Of course as above, the visa versa of these ratios are also true. Hence, according to the above, tungsten ($\alpha = 4.6$) could well be used for balancing tin ($\alpha = 23$) on 51710 steel ($\alpha = 13$), e.g. a ratio of $4.6:23 = 1$ to 5 for the balancing element α to coating α and $23:13 = 1.76:1$ for the coating α to substrate α .

The particular coating and balancing metal or element may be chosen as desired so long as the above requirements are met. A few simple tests will determine a suitable ratio for balancing the coating plus balancing metal or element α with the substrate α . Hence, after determining the α of the substrate, various ratios of coating and balancing metal or element are prepared and the resulting α thereof is determined. When the resulting coating α is with about ± 40 percent, especially ± 20 percent, e.g. ± 10 percent, of the α of the substrate a suitable combination of coating and balancing metal or element has been obtained for the particular substrate of course, simply balancing the α 's does not mean that the coating will provide good oxidation protection, but where elements which provide good oxidation resistance are used, the balancing of such elements will provide a much better protective coating than where this technique is not used.

Particularly important is the use of silver, tin and aluminum, or alloys of these three metals for diffusing into steels with silicon as the balancing element. These have great commercial importance and the invention will be further illustrated in connection therewith, although the invention is fully applicable to the above.

The coating and balancing metals or elements are conveniently diffused into the substrate from a compound thereof. The particular compound is not important so long as it has a melting point lower than the melting point of the substrate and so long as other deleterious elements from the compound are not co-diffused with the metallic atom. Many such suitable dif-

fusion compounds are well known to the art, as disclosed in the above noted patents and one skilled in the art can readily choose a suitable compound. Generally the salts and oxides are the most convenient compounds to use, especially since they present no problem of co-diffusion, as noted above. For example, BaI Si_4 or $\text{Na}_3 \text{AlF}_6$ are convenient compounds for supplying the aluminum atoms for the coating and the silicon atoms for the balancing agent. As will be shown below, the $\text{Na}_2 \text{AlF}_6$ can also serve a dual function for supplying the element of a large atom size, i.e. sodium in this case, for mitigating voids in the crystal structure.

In this latter regard, the element for mitigating voids should have an atomic volume of at least 9 W/D such as molybdenum and above, and preferably at least 20, e.g. Na, K, Rb, Cs, Ca, Sr, Ba, Te, I, etc. Here, again, however, the particular compound of the large atomic volume element is not important so long as it has a melting point below that of the substrate to be coated. Here again, one skilled in the art may readily choose a suitable compound, although the salts and oxides are the more convenient compounds. With regard to the particular balancing metal or element compound, the coating compound and the large atomic volume compound, one need only to consult standard hand books and textbooks to choose suitable compounds and no further explanation thereof is required for one skilled in the art.

The amount of the large atomic volume atom will of course depend on the amount of voids to be filled, but since the voids will be relatively small in total substrate and coating, generally less than 10 percent especially about 8 percent, e.g. 5 percent or less of the total coating composition are suitable amounts. With these small amounts the thermal expansion of the coating composition is not greatly effected by the large atomic volume atom and its effect thereon may be ignored. The coating with the balancing metal or element along with the element of large atomic volume may be applied to the substrate from any desired compounds thereof, as noted above, by heating the substrate in contact with the coating (including the balancing metal or element and the large atomic volume element) for a sufficient time to cause diffusion of the coating into the substrate. Preferably the heating is carried out in an inert atmosphere, e.g. nitrogen, but more preferably in a reducing atmosphere, e.g. hydrogen, at a temperature above the melting point of the coating and below the melting point of the substrate, e.g. from 500°F to $3,000^\circ\text{F}$ for at least one minute up to 10 hours or more. Conveniently, the compounds which provide the coating (including the balancing metal or element and the element of large atomic volume) are initially applied to the substrate with any convenient binder, e.g. a non-carbonizing plastic, glue, dope, etc., but ethyl silicate or hydrolyzed ethyl silicate is especially useful. The silicon atom (when this is the balancing atom) can be obtained, at least in part, therefrom. The diffusion process, itself, and suitable binders are well known to the art and no further explanation is necessary.

The invention will be illustrated by the following examples which are directed to the best modes, but it is to be understood that the invention is fully applicable to the foregoing disclosure.

EXAMPLE 1

A thick slurry was prepared of the following ingredients:

BAISi ₄	75 grams
NaAlF ₆	25 grams
hydrolyzed ethyl silicate	50 ml.

A mild steel rod was brushed clean and the slurry applied thereto by dipping. The takeup of the slurry was about 10 mils thick. After drying at 150°F for 30 minutes, the rod with the coating therein was heated in a hydrogen atmosphere for one-half hour at 2,050°F and thereafter post soaked in a hydrogen atmosphere for five hours at 1,600°F. The rod was cooled and brushed clean. The rod was cycled between 80°F and 1,000°F for 20 days (approximately two hours per cycle) and no evidence of deterioration of the aluminum coating was noted.

EXAMPLE 2

The procedure of example 1 was repeated, except only AlF₃ in polyvinyl alcohol binder was used. The resulting aluminum coated rod was cycled as in example 1 but after 20 days, the coating showed cracks, spalling and general deterioration.

EXAMPLE 3

Similar to Example 1, another slurry was prepared using a mixture of molybdenum trioxide, manganese dioxide in a ratio of 19:1 with a 5 percent pyroxylin-acetone vehicle. This was sprayed on a substrate of nickel base super alloy (Inco 713). This was dried and then followed with a mixture of 19 parts aluminum powder, 1 part silicon, 3 parts NaAlF₆ in a vehicle of hydrolyzed ethyl silicate. This was dried at 250°F. and then placed in a reducing atmosphere (hydrogen) at 1900°F., followed by an aging treatment of six hours at 1600°F. in an air atmosphere. Results similar to Example 1 were obtained.

The particular substrate is not critical and may be as desired. Of course, steel is the most commercially important but magnesium, titanium, nickel, cobalt and

their alloys may be used.

What is claimed is:

1. A diffusion coated substrate comprising a metallic substrate and a diffusion coating composition thereon, said diffusion coating composition containing:
 1. a coating metal or element;
 2. a balancing metal or element; and
 3. an element of large atomic volume; the ratio of the coefficient of thermal expansion of the said balancing metal or element to the coefficient of thermal expansion of the said coating metal or element being at least 1:2, or visa versa, the atomic volume of the large atomic volume element being at least 20 W/D; and the proportion of the said coating metal or element to the proportion of balancing metal or element being so chosen that the resulting diffusion coating composition has a coefficient of thermal expansion substantially the same as that of the said metallic substrate.
2. The product of claim 1 wherein the said ratios of coefficients of thermal expansion of the coating metal or element to the balancing metal or element are at least 1:3 or greater.
3. The product of claim 1 wherein the ratios of the coefficient of thermal expansion of the said coating metal or element to the coefficient of thermal expansion of the said substrate, or visa versa, are less than 5:1.
4. The product of claim 3 wherein the said ratios of coefficients of thermal expansion of the coating metal or element to the said substrate are less than 2:1.
5. The product of claim 1 wherein the amount of the large atomic volume element is 10 percent or less of the coating composition.
6. The product of claim 1 wherein the substrate is a steel, the coating metal is selected from silver, tin and aluminum, the balancing element is silicon and the large atomic volume element is sodium.
7. The product of claim 6 wherein the coating metal is aluminum, and both the aluminum and the silicon are supplied from BAISi₄ and the sodium is supplied, at least in part, from Na₃AlF₆.

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