

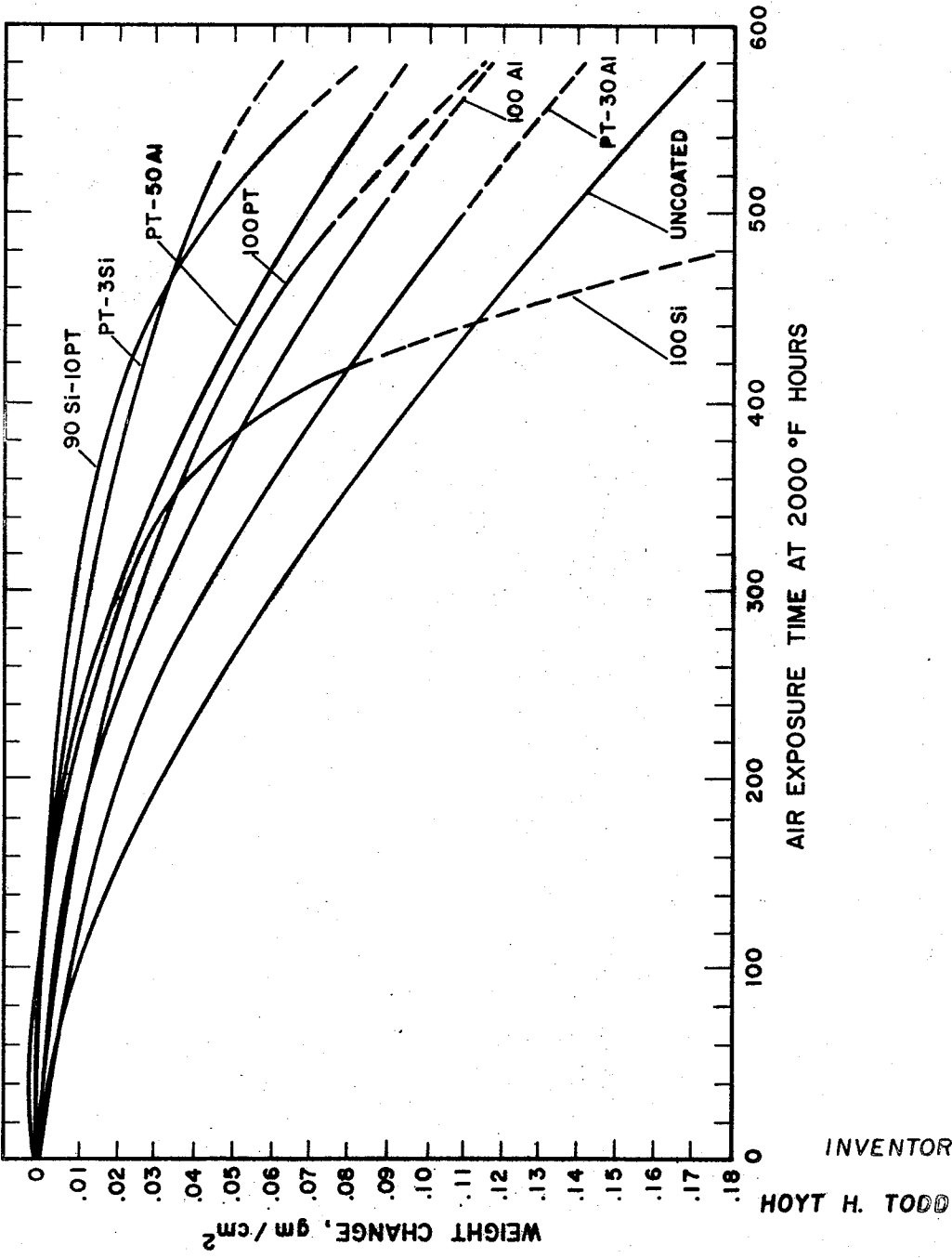
Feb. 10, 1970

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3,494,748

OXIDATION RESISTANT COATING AND ARTICLE

Filed Dec. 16, 1966



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3,494,748

OXIDATION RESISTANT COATING AND ARTICLE
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Filed Dec. 16, 1966, Ser. No. 602,268

Int. Cl. B23p 3/20; C23c 3/00

U.S. Cl. 29—194

3 Claims

ABSTRACT OF THE DISCLOSURE

A method of forming a high temperature, oxidation resistant structural member by coating a metal structural member with an impermeable layer consisting essentially of an alloy of platinum and at least one other oxidation resistant element and the article produced by such method. The presently preferred other oxidation resistant element is silicon although aluminum, chromium, and other oxidation resistant element may be used along with other metals.

BACKGROUND OF THE INVENTION

One of the limiting factors in the design of advanced power plants such as jet engines and other structures subjected to high temperatures, e.g., above about 1800° F., has been the development of materials exhibiting a combination of adequate strength, oxidation resistance, and creep resistance at such high temperatures. Attempts to optimize oxidation resistance and the desired mechanical properties within the same alloy system have been unsuccessful. For example, those alloying elements which increase resistance to high temperature creep, e.g., columbium, tungsten, molybdenum, and vanadium, detract from oxidation resistance when added to alloy systems having inherently good oxidation resistance. Consequently, composite materials have been used wherein two or more materials are combined in such a manner so as to utilize the optimum characteristics of each. Considerable progress has been made in the production of such composite materials wherein a material having a high mechanical strength and creep resistance is clad with a thin layer or coating of material exhibiting excellent oxidation resistance. Examples of such coatings are diffusion coatings of aluminide, silicide, and beryllide which are formed by diffusion at high temperature from the vapor phase. However, such coatings have a number of disadvantages such as low thermal and mechanical shock resistance. Consequently, repeated high temperature cycling or mechanical shock may result in spalling. Such spalling tendency is further accentuated by a mismatch of expansion coefficients between the coating and the base material. Furthermore, such coatings still encounter substantial oxidation problems at high operating temperatures. Examples of currently used coatings are described in U.S. Patents Greene, et al., 2,970,065; Hanink, et al., 3,000,755; and Joseph, 3102044.

DESCRIPTION OF THE INVENTION

Consequently an object of the present invention is a high temperature, high mechanical strength, oxidation resistant structural member.

Still another object of the present invention is a high temperature, high mechanical strength, metal structural member having an impermeable layer on said member consisting essentially of an alloy of platinum and at least one other oxidation resistant element and the method of coating such member.

Other objects and advantages of the present invention will be readily apparent from the following description and drawing which illustrate both a preferred embodiment

of the present invention as well as other embodiments of the present invention.

In order to facilitate understanding of the present invention, reference will be made to the appended drawing of the test results of the preferred specific embodiment of the present invention as well as other embodiments of the present invention. Such drawing should not be construed as limiting the invention, which is properly set forth in the appended claims.

In the drawing:

FIG. 1 shows the relationship between the weight loss of various test samples with respect to the air exposure time at 2000° F.

As set forth above, the article of the present invention involves the combination of a high temperature, high mechanical strength, metal structural member and an impermeable layer on said member consisting essentially of an alloy of platinum and at least one other oxidation resistant element. In the preferred embodiment of the present invention, such structural metal member is the turbine blade used in the various types of gas turbine engines. As employed herein, the term "turbine blade" includes turbine rotor buckets, nozzle guide vanes, and stator blades since these are all components of gas turbine engines which are exposed to high operating temperatures particularly in the axial flow type of gas turbines. The metal which may be used to form such high temperature, high mechanical strength, structural member may be any of the commonly known alloys employed for such applications such as the nickel-base and cobalt-base alloys. Examples of such alloys are Inconel-X as well as the examples set forth in the aforementioned Greene and Hanink patents.

The impermeable layer on said member consists essentially of platinum and at least one other oxidation resistant element, i.e., elements such as aluminum, chromium, magnesium, silicon, cobalt, tantalum, or titanium. The weight concentration of platinum in said layer may be in the range of about 5% to 97%. The preferred concentration range is about 5% to 50% by weight of platinum, and the preferred concentration is about 10% by weight when the other element consists essentially of silicon. When the remaining element consists essentially of aluminum, the preferred concentration range of the platinum is about 30% to 60% by weight and the preferred concentration is 50% by weight.

The method of forming the article of the present invention comprises coating a high temperature, high mechanical strength, metal structural member with an impermeable layer consisting essentially of an alloy of platinum and at least one other oxidation resistant element. A variety of coating techniques may be utilized to deposit such layer on the structural member such as plating from a liquid, reaction deposition, direct vapor deposition, hot spraying, and cladding and slurry diffusion, i.e., dipping, spraying, or brushing. Some of such coating techniques are described in the aforementioned Hanink patent. However, the presently preferred technique for coating the layer on a structural member involves forming a well mixed dispersion of the alloying ingredients in a liquid vehicle, hand painting such dispersion on the surface of the structural member, and then heating to form an impermeable coating. Such technique is described in more detail along with the method of testing the resulting article in the following examples.

EXAMPLES

A platinum powder is prepared by the hydrazine reduction of chloroplatinic acid solution. Silicon powder was prepared by agate milling of single crystal silicon until it passed through a -325 mesh screen. Other components utilized such as MoSi₂, Cr, high carbon Ferro-

Silicon, and Al came in powder form of -100 mesh or smaller and so were added directly in such form. The resulting powders were then added as a mixture in the proportions noted in Table 1 to an agate mortar. Next, benzyl alcohol in the amount of 30% by weight of the powder mixture was added to the agate mortar. Then a uniform dispersion of the powders in the benzyl alcohol was prepared by hand milling. The resulting alloy dispersion was applied to a specimen surface by hand painting. The specimen was a sample of Inconel-X having the dimensions of 2 x 1/2 x 1/8 inches cut from a rolled sheet. The coated specimen was then dried at 120° C., and then placed in a vacuum furnace and heated to 1200° C. for 30 minutes at a pressure of 1×10⁻⁵ mm. Hg. Such coating procedures was repeated three times for each test specimen to insure a continuous coating of reasonable thickness with three test specimens being thus coated. Upon the completion of the coating operation, the specimens were weighed and the coating weight and thickness were calculated and formed to have an average weight and thickness as specified in Table 1.

After weighing, the three specimens were placed in an open air furnace at 2000° F. and positioned to expose all surfaces of the specimen to the atmosphere. The specimens were removed from the furnace approximately every 50 hours and allowed to cool. After cooling, all loose scale was removed from the specimen's surface by lightly brushing with a brass bristle brush. The specimens were then weighed and the progressive total weight loss plotted against time as shown in the figure. At the end of the 500-hour test interval, weight loss and oxidation depth were measured as set forth in Table 1 and then all scale was removed by vapor honing and the specimens were again weighed and the weights plotted on a chart as a measure of any discrepancy which might have occurred as a result of adherent areas of scale. Such latter procedure does not alter the relative standings of the coatings with regard to oxidation rates.

TABLE 1

Weight loss at 500 hours (gm./cm. ²)	Powder composition (percent by weight)	Coating weight (gm./cm. ²)	Coating thickness (inches)	Oxidation depth at 500 hours (inches)
0.1530	Uncoated			0.0073
0.0988	100 Pt.	0.02935	0.00054	0.0047
0.0585	97 Pt-3 Si	0.01800	0.00036	0.0026
0.0422	10 Pt-90 Si	0.00345	0.00058	0.0020
(1)	100 Si	0.00302	0.00051	(2)
0.1210	70 Pt-30 Al	0.00140	0.00035	0.0058
0.0753	50 Pt-50 Al	0.00074	0.00024	0.0036
0.1450	100 Al	0.00032	0.00048	0.0116

¹ 0.07 gm./cm.² at 44 hours—weight loss then became so great that test was discontinued.

² Not calculated.

In addition to the quantitative measurements on the foregoing compositions, semi-quantitative measurements have been made on the following compositions and such compositions were found to achieve comparable results:

10 Pt—25.9 Si—44.1 Mo—14 Cr—6 Fe
 10 Pt—33.3 Si—56.7 Mo
 10 Pt—22.2 Si—37.8 Mo—20 Al—10 Co
 10 Pt—14 Cr—5 Fe—44 Mo—1 C—26 Si
 10 Pt—20 Al—10 Co—38 Mo—22 Si
 14.2 Pt—14.2 Cr—27 Mo—16 Si—28.6 Al

Many other specific embodiments of the present inventions will be obvious to one skilled in the art in view of this disclosure. For example, minor additions of other metals may be added to increase the coating lifetime. Examples of such metals which may be utilized are cerium, thorium, calcium, and zirconium as well as alloys of one or more of such metals. Likewise, metals such as molybdenum and tungsten may be added to increase resistance to sulfidation, although such additives may reduce resistance to oxidation.

The following theory may explain the operation of the present invention; however, it is not intended that the present invention be limited to such theory since other theories are possible. Such theory should be regarded as merely a probable explanation for the unusual and unexpected results achieved by the present invention and not as a limitation upon the invention. It is well known that the resistance to oxidation of the high temperature, high mechanical strength alloys such as Inconel-X is achieved by forming an oxide film which retards diffusion. Thus, the oxidation process begins at the gas/metal interface and a modified surface layer is immediately formed. Further reaction then proceeds by the mechanisms of diffusion which include surface, boundary, and volume modes with the predominant mode depending upon the composition, structure, and temperature of the system. It is further generally accepted that the diffusion of atoms or ions in inorganic compounds occurs through interstitial or vacant lattice sites with concentration gradients supplying the necessary energy potential. For example, at low temperatures metal ions are normally unable to diffuse through the oxide film. But electrons are presumably capable of moving from the substrate metal to the absorbed oxide film either by thermionic emission or by the tunnel effect. Such migration of electrons produces cations at the metal-oxide interface and oxygen anions at the oxide-gas interface. This process, in turn, creates energy potential necessary to move the cations outward or anions inward through the film. Thus, before oxygen can diffuse through the oxide layer, it must be in atomic or ionic form. However, the coating of the present invention includes a platinum as an essential constituent and platinum catalyzes the formation of molecular oxygen from atomic or ionic oxygen. Thus, when the atomic or ionic oxygen is formed in the oxide layer, platinum retards its diffusion by converting it to its molecular form. Furthermore, since pure platinum coating does not produce substantially improved oxidation resistance over presently available coatings, it appears that the platinum constituent must be deposited with at least one other oxidation resistant element such as aluminum, silicon, or chromium in order to achieve the improved oxidation resistance.

There are many features of the present invention which clearly show the significant advance the present invention represents over the prior art. Consequently, only a few of the more outstanding features will be pointed out to illustrate the unexpected and unusual results obtained by the present invention. As illustrated in the figure and Table 1, the uncoated, high temperature, high strength metal such as Inconel-X has relatively poor oxidation resistance, but it can be substantially improved by the addition of a pure aluminum coating or a pure platinum coating. However, as set forth in the present invention, even such improved oxidation resistance can be very substantially increased simply by combining platinum with at least one other oxidation resistant element such as aluminum, silicon, or chromium. For example, in the case of silicon, the oxidation resistance is at least approximately doubled.

It will be understood that the foregoing description and examples are only illustrative of the present invention, and it is not intended that the invention be limited thereto. All substitutions, alterations, and modifications of the present invention which come within the scope of the following claims or to which the present invention is readily susceptible without departing from the spirit and scope of this disclosure are considered part of the present invention.

I claim:

1. A high temperature, high mechanical strength, oxidation resistant structural member comprising: a high temperature, high mechanical strength, metal structural member and an outer impermeable layer, said outer layer comprising about 10% to about 97% platinum with the balance silicon.

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2. The structural member of claim 1 wherein said alloy comprises about 10% platinum and about 90% silicon.
 3. The structural member of claim 1 wherein said alloy comprises about 3% silicon and about 97% platinum.

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U.S. Cl. X.R.

29—197, 198; 117—22, 131