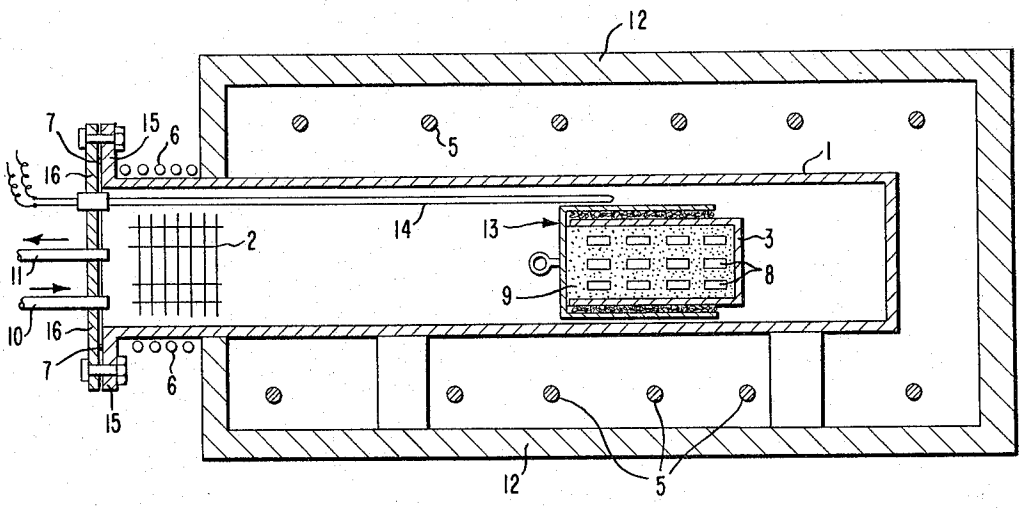
Dec. 6, 1966 L. A. MONSON 3,290,126

PROTECTIVELY COATED NICKEL OR COBALT ARTICLES AND PROCESS OF MAKING

Filed April 29, 1965 4 Sheets-Sheet 1

FIG. 1



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FIG. 2

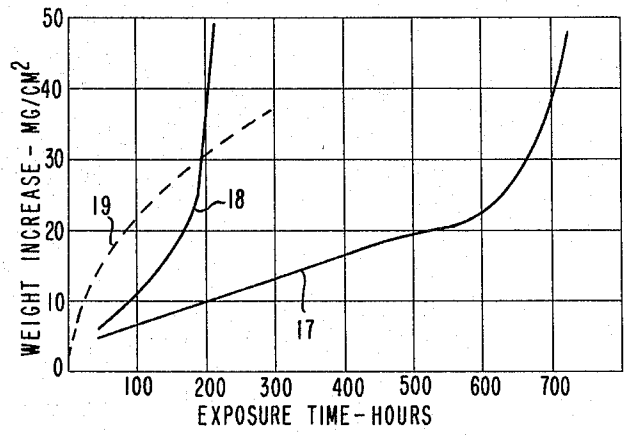


FIG. 4

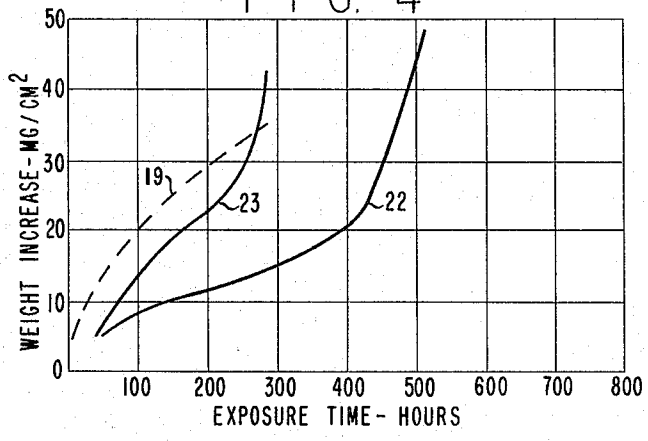
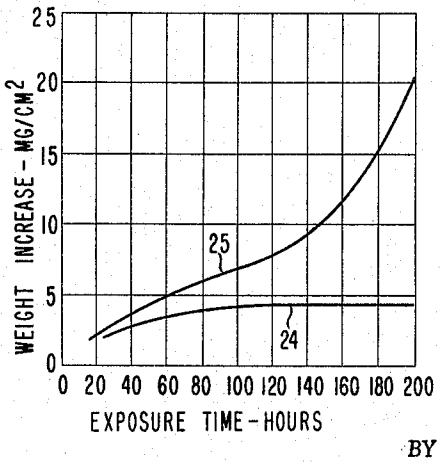


FIG. 6

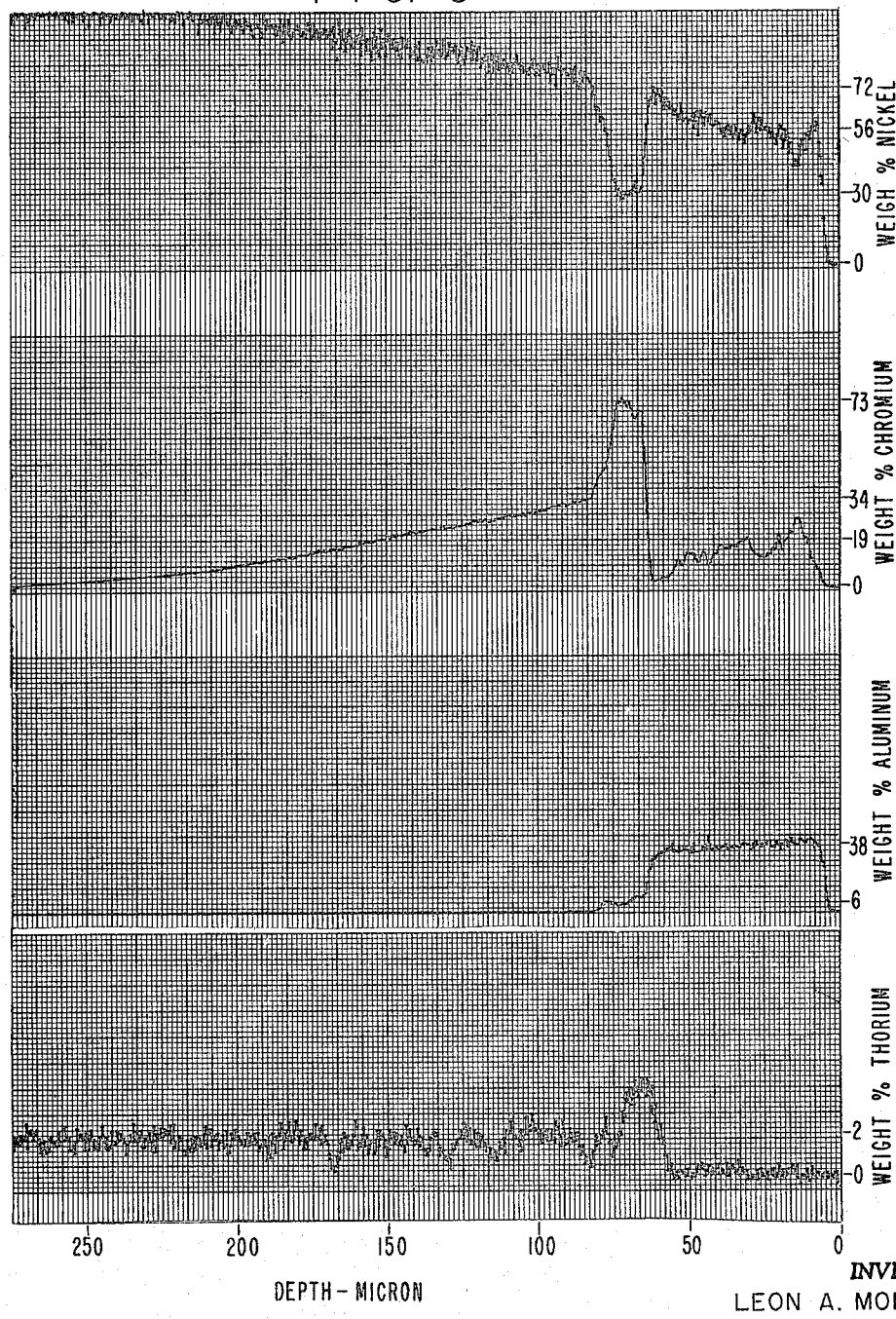


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FIG. 3

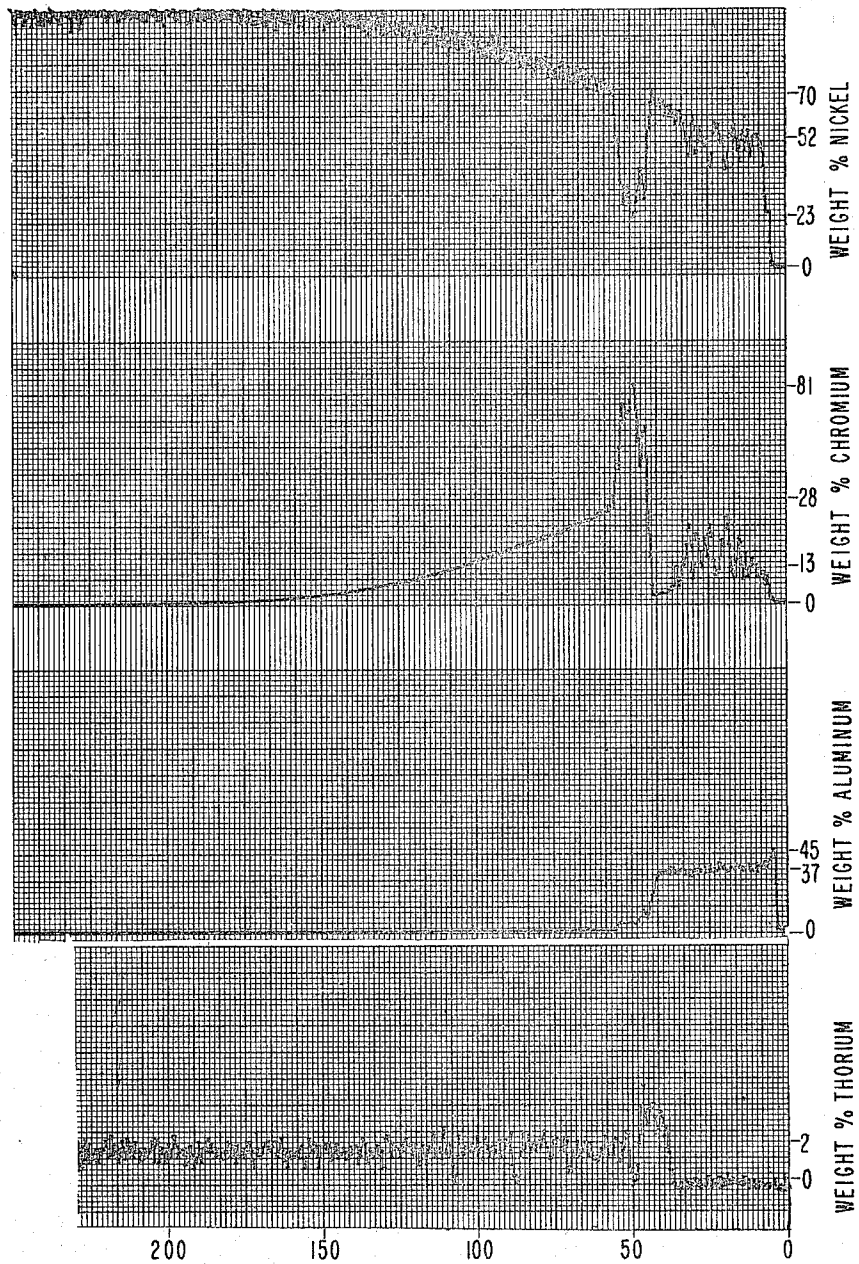


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FIG. 5



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United States Patent Office

3,290,126

Patented Dec. 6, 1966

3,290,126

PROTECTIVELY COATED NICKEL OR COBALT ARTICLES AND PROCESS OF MAKING

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Filed Apr. 29, 1965, Ser. No. 451,823
7 Claims. (Cl. 29—194)

This invention relates to processes for applying protective coatings to dispersion-modified metals, especially to nickel and nickel-base alloys dispersion-modified with thoria to increase the resistance of such metals to oxidation when exposed to high temperatures for long periods, and to the products of these processes.

More particularly the invention is directed to the steps in such processes comprising (1) forming on a dispersion-modified nickel-base alloy surface a first coating comprising chromium alloyed with nickel and (2) forming upon said first coating a second coating comprising aluminum alloyed with chromium and with nickel and nickel-chromium alloy from the first-formed coating. The invention is further directed to the so-produced coatings having certain hereinafter defined compositions which are valuable in protecting dispersion-modified nickel and nickel-base alloys against oxidation when such metal and alloys are exposed to oxidizing conditions at elevated temperatures.

In the drawings:

FIGURE 1 shows in cross-section an apparatus suitable for carrying out a process of the invention, and

FIGURE 2 is a graph showing the protection afforded to a base metal by coatings of the invention at 2200 and 2400° C., and

FIGURE 3 is a microprobe tracing, showing the composition of a coating of the invention in relation to depth, and

FIGURE 4 is another graph showing the protective effect of coatings of the invention produced by a process different from that used in FIGURE 3, and

FIGURE 5 is another microprobe tracing, showing the composition of another coating of the invention in relation to depth, and

FIGURE 6 is another graph showing the protective effect of coatings produced by still another process of the invention.

Metals which have been strengthened by dispersions of refractory oxides, carbides, nitrides, borides, etc., have recently been finding increasing importance as structural materials. One of these has been a dispersion-modified nickel in which the strengthening dispersion is 2 volume percent submicron thoria uniformly dispersed in the nickel. Although nickel-base alloys, generally known as "superalloys," are well known for their superior strengths at temperatures up to, say 2000° F., and also in many cases show superior resistance to oxidation at even higher temperatures, most of these alloys show decreasing strength in elevated temperature ranges where dispersion-modified metals, and especially nickel dispersion-modified with thoria, exhibit superior strength properties. Also, in contrast to superalloys, nickel modified with dispersed thoria does not exhibit the property of internal oxidation which characterizes many of the superalloys. Although dispersion-modified nickel-base alloys exhibit superior strength at elevated temperatures, their rates of oxidation

at these temperatures are higher than might be desired. This oxidation results in a gradual reduction of load-bearing area by conversion of the metal to oxide. For uses which involve long exposure time in extremely oxidizing environments, protective coatings offer a way to minimize the oxidation rate of these strong dispersion-modified alloys.

Two coating methods have been proposed for protecting dispersion-modified nickel from oxidation at elevated temperatures. The first is known as "aluminizing," in which an aluminum coating is applied for the protection of the underlying base metal, and the second as "chromizing, in which a coating of chromium is applied for the same purpose. Some of the coatings applied by aluminizing have shown extremely low oxidation rates during static exposure tests at 2000° F. or above; however, for practical applications it is necessary that the oxidation-resistant coating be and remain firmly adherent under cyclic testing conditions at temperatures at least as high as 2200° F., and, unfortunately, coatings applied by aluminizing are deficient in this regard. Where aluminum coatings have been applied directly to dispersion-modified nickel-base alloys, these coatings have been found in most cases to be porous or to become porous upon heating, so that the aluminide coating spalled off. This spalling appears to be associated with "line" porosity at the interface of the coating and the metal base material, with subsequent loss of the coating and rapid or even catastrophic oxidation of the underlying alloy.

The porosity which is so damaging may be due to diffusion phenomena. Its formation is increased or aggravated by the oxide particles present in the dispersion strengthened materials. Other nickel or cobalt-base superalloys can be protected by a single-step aluminized coating. Reasons for this, contrasted with the corresponding failure in dispersion strengthened alloys, may include the following:

(1) Service temperatures are generally lower than those proposed for oxide dispersion strengthened alloys;

(2) Superalloys do not contain the stable oxide dispersoid particles which may nucleate porosity; and

(3) Superalloys contain elements which may prevent or retard diffusion-induced porosity as well as that resulting from other mechanisms.

The protection of dispersion-modified nickel or nickel-base alloys by chromizing has been somewhat successful under certain conditions. However, the degree of protection obtained by the formation of a chromium-bearing alloy varies greatly with the chromium content of the coatings. Since the chromizing process is dependent upon diffusion of chromium into the nickel-base underlying alloy, there always exists a chromium gradient in the coating alloy composition, and there are present chromium-bearing alloys of such low chromium concentration that protection of the basis metal is minimized. As diffusion occurs, the chromium concentration falls to a point at which the oxidation is greatly accelerated and may become catastrophic.

Now according to the present invention it has been found that adherent, highly oxidation-resistant protective coatings can be applied to dispersion-modified nickel and nickel-base alloys by a process which comprises the steps of (1) first forming a diffused layer of chromium with the base alloy, and (2) subsequently forming an additional diffused layer of aluminum with the first-formed,

diffused, chromium-bearing layer and the underlying base alloy.

More particularly the invention is directed to novel articles comprising (1) a body of a metal matrix selected from the group consisting of (a) at least one metal of atomic numbers from 27 to 28, inclusive, and (b) alloys in which there is at least 50% by weight of at least one metal of atomic number from 27 to 28, inclusive, alloyed with at least one Group VI–B metal of atomic number below 75, said matrix metal being dispersion-strengthened with a particulate refractory metal oxide having a free energy of formation at 1000° C. greater than 100 kilocalories per gram atom of oxygen, (2) a triplex coating adherently bonded to and integral with said first body, said coating comprising (a) an inner diffusion zone comprising an alloy of said matrix metal with an increasing concentration of chromium up to about 50% by weight in the outwardly direction, (b) a second zone, outward of zone (a), comprising an alloy of said matrix with about 50 to 95% by weight of chromium and up to 10% by weight of aluminum and having said particulate refractory oxide dispersed therein, and (c) an outer zone comprising an alloy of at least one metal of atomic number from 27 to 28, inclusive, containing, by weight, about from 10 to 50% of aluminum and 2 to 30% of chromium.

The invention is further particularly directed to processes for producing the just-described coated articles, said processes comprising the steps of preparing an uncoated article comprising a metal matrix selected from the group consisting of (a) at least one metal of atomic number from 27 to 28, inclusive, and (b) alloys in which there is at least 50% by weight of at least one metal of atomic number from 27 to 28, inclusive, alloyed with at least one Group VI–B metal of atomic number below 75, said matrix metal being dispersion-strengthened with a refractory metal oxide having a free energy of formation at 1000° C. greater than 100 kilocalories per gram atom of oxygen, and subjecting said article to the steps comprising (1) effecting contact between such article and a uniform mixture comprising, by weight, about 5 to 90% of chromium metal, 0.05 to 5% of a transfer agent selected from the group consisting of (A) iodine and (B) volatile halides of alkali metals, and (C) volatile halides of ammonia, the balance of the mixture being inert material selected from the group consisting of alumina, zirconia, silica and thoria, at least the chromium and inert material being particulate and having a size small enough to pass through a 60-mesh sieve (U.S. Standard), (2) heating, while maintaining such contact, in an environment which is inert except for the presence of such transfer agent, at a temperature in the range of about from 2000 to 2450° F., whereby chromium is deposited upon and diffused into said article, and continuing such contact and heating until between 0.005 and 0.100 g./cms.^{2} of chromium has been deposited, and (3) thereafter effecting contact of the product of step (2) with a mixture comprising, by weight, about from 0.5 to 20% of −60 mesh aluminum metal, and about from 0.05 to 0.5% of a transfer agent of the group of step (1), the balance of the mixture being −60 mesh inert of step (1), and (4) heating while maintaining such contact, at a temperature in the range from 1000 to 2300° F. for about from 0.5 to 36 hours at atmospheric pressure.

The coatings of this invention consist of three principal zones, described in an inward-moving direction (illustrated in FIGURES 3 and 5) as follows:

(1) Outer zone consisting of one or a mixture of aluminide compounds of Ni with Cr or of Co with Cr (based principally on NiAl or CoAl);

(2) An intermediate zone based on body-centered cubic solid solution of nickel and Al in Cr; and

(3) An inner zone of face-centered cubic solid solution of chromium in nickel.

It is important that materials subjected to erosion-type service have coatings which are erosion resistant. It is obvious that the presence of liquid coating phases during service would be disastrous. For this reason Al or Al_3Ni phases must be avoided.

FIGURE 1 of the drawings shows a cross-sectional diagram of a furnace **12** which can be used to carry out a process of this invention. Extending into the furnace is a 6"-diameter Inconel tube **1**, fitted with flange **15** and faceplate **16**, enclosing a 4"-diameter cementation pack container **3** preferably constructed of nickel. Within the container are specimens **8** to be coated, packed in a cementation mix **9**. The container **3** is fitted loosely into an outer shell **13** and held in place by a packing of silica wool **4**. The temperature in the furnace is measured by a thermocouple **14**. Heat is supplied to the furnace by electrical resistance heating elements **5**. A radiation shield **2** of stainless steel is located at the end of the Inconel tube; the exterior of the tube in this area is cooled by cooling coils **6**. Gas inlet line **10** and outlet line **11** are used, respectively, to introduce gas to the tube or to evacuate it. The faceplate is sealed to flange by ring **7**.

Example 1

Ten coupons ½" x 1" x 0.060" were cut from a sheet of a nickel-thoria alloy (nickel-2 volume percent ThO_2) known commercially as TD Nickel. These coupons were packed, separately from each other, in a nickel container of the configuration shown as **3** in FIGURE 1, using as pack material a mixture of 30-weight percent powdered alumina (−100 mesh particle size), 65-weight percent powdered chromium (also −100 mesh particle size), and five-weight percent potassium fluoride. This packed container was fitted into an outer container, the space between the inner and outer containers being packed with silica wool.

The container and contents were heated at 2300° F. for 24 hours in vacuum. The vacuum was maintained at 5×10^{-5} mm. Hg throughout the heating period. After 24 hours, heating was discontinued and the samples were cooled to room temperature in the pack, while still under vacuum.

The ten coupons were removed from the chromizing pack and were observed to have a smooth metallic coating of dull sheen. The chromized samples were weighed and found to have gained an average of 0.040 g./cm.^{2} by deposition of chromium from the pack.

The ten coupons were packed again in the same container and treated by the following aluminizing process: The pack consisted of 4% by weight powdered aluminum (−100 mesh particle size), 0.1% by weight ammonium chloride, and 95.9% by weight alumina (−100 mesh size). A flow of inert gas, argon, was introduced into the furnace, and this flow was maintained throughout the heating time, which was five hours at 1750° F. After this heating the flow of inert gas was continued while the pack was cooled to room temperature. The pack was then opened and the coupons removed.

The ten coupons were weighed and were found to have gained an average of 0.0134 g./cm.^{2} by deposition of aluminum. One coupon was reserved for analytical tests, and the nine remaining coupons were subjected to cyclic tests for oxidation resistance as follows:

Eight coupons were heated in flowing air, four at 2200° F. and four at 2400° F., held at temperature for one hour, and cooled in air to room temperature. The cycle was then repeated until specimen failure. The termination in lifetime of each sample was considered to be the time at which a greatly accelerated increase in weight was noted. In FIGURE 2 there is plotted increase in weight as a function of time for the coupons prepared according to this example; line **17** shows results of tests at 2200° F.; line **18** shows results of tests at 2400° F.; line **19** shows results of tests on uncoated TDNi at 2200° F. The lifetime of the coated coupons was adjudged to be 624 hours at 2200° F. and 175 hours at 2400° F.

The coupon reserved for analytical testing was cross-sectioned and subjected to microprobe analysis to determine the composition of the coating. FIGURE 3 shows the microprobe tracing obtained over the cross section of the coated coupon. The outer edge of the coating is indicated as **0**; the depth of sample therefore extends toward the left margin. The reference marks are in 50μ units. For convenience, certain percentage levels of Th, Al, Cr and Ni are marked. It will be noted that although there has been considerable diffusion of chromium into the basis metal, the level of aluminum is constant at about 38% through the major portion of the coating, and falls off rather quickly at a depth of about 55μ to a level of about 6%.

Example 2

Ten coupons ½" x 1" x 0.060" of TD-nickel of the same lot as used in Example 1 were coated as follows:

The samples were packed in the nickel container of Example 1, using a chromizing pack consisting of, by weight, 20% chromium of −100 mesh particle size, 0.5% NH_4Cl, and 79.5% alumina of −100 mesh particle size. The pack was placed in the furnace and an atmosphere of inert gas at atmospheric pressure was maintained within the furnace while the pack was heated for 24 hours at 2250° F. The pack was then cooled in the furnace while still under flow of inert gas. The coupons at room temperature were removed from the pack and weighed. They were found to have gained an average of 0.0336 g./cm.^{2} by chromium deposition.

The coupons were next subjected to further coating by the aluminizing process of Example 1, the aluminizing pack being as therein described. The gain in weight of the coupons was almost identical to the gain of the coupons in Example 1. The coated coupons were subjected to oxidation testing, one coupon being reserved for microprobe analysis. The lifetime of the coated coupons was found to be 456 hours at 2200° F. and 200 hours at 2400° F.

The results of oxidation testing of these samples is shown graphically in FIGURE 4. In this figure weight gain is plotted as a function of exposure time. Tests at 2200° F. are shown in line **22**; tests at 2400° F. are shown as line **23**. For comparison, the results on uncoated TD Nickel are again shown as line **19**.

The sample which was reserved for microprobe analysis was cross-sectioned, and a microprobe tracing run on the cross section of each coupon. This tracing is shown in FIGURE 5. The outer edge of the coupon is indicated as **0**. The depth of the sample is indicated in units of 50μ.

Example 3

This example illustrates the coating of a nickel-11.5 weight percent molybdenum-0.2 weight percent zirconium-2 volume percent thoria alloy by a process of this invention.

Four coupons, each ½" x 1" x 0.060", were coated by first placing them at points of maximum inter-coupon spacing, in a pack comprising, by weight, 5% KF, 52.5% Al_2O_3 (−100 mesh particle size), and 42.5% chromium metal (−200 mesh particle size). The pack was heated for 24 hours at 2350° F. under vacuum to chromize the coupons. The coupons were then removed and found to have gained an average of 0.0706 gms./cm.^{2}.

The four chromized coupons were again placed in a pack, the pack now comprising, by weight, approximately 5% powdered aluminum metal (−100 mesh particle size), 0.1% NH_4Cl, and 94.9% alumina (−100 mesh size). The pack was heated for 2 hours at 1900° F. in an inert gas atmosphere to aluminize the coated coupons. The pack was then cooled and the coupons were removed. They were found to have gained an average of 0.0092 gms./cm.^{2}.

Cyclic oxidation tests were carried out by heating these four coupons in flowing air for one-hour periods and cooling to room temperature. The following weight increases were found:

Total hours exposure time	Cumulative weight increase (average for 4 coupons) milligrams/cm.^{2}
20	1.9
40	2.8
60	3.5
80	3.9
100	4.3
120	4.3
140	4.3
160	4.3
180	4.3
200	4.3

Example 4

Four additional coupons of the alloy used in Example 3 were chromized and aluminized under the following conditions:

For the chromizing, four coupons were placed in a pack comprising, by weight, 4.8% KF, 17.6% alumina (−100 mesh), and 77.6% chromium metal powder (−200 mesh). The pack was heated for 24 hours at 2200° F. in vacuum, then cooled, and the four coupons removed. They were found to have gained an average of 0.0431 gms./cm.^{2}.

The chromized coupons were placed in a pack comprising, by weight, approximately 5% aluminum metal (−100 mesh size), 0.1% NH_4Cl, and 94.9% alumina (−100 mesh size). The pack was heated in an inert atmosphere for one hour at 2200° F. The coupons, cooled and removed from the pack, were found to have gained an average of 0.0227 gms./cm.^{2}.

These four chromized and aluminized coupons were tested for their resistance to oxidation by exposing them to a flow of air at 2200 F. for one-hour periods. The following (average) gains in weight were noted:

Total hours exposure time	Cumulative weight increase (average for 4 coupons) milligrams/cm.^{2}
20	2.3
40	3.8
60	4.7
80	5.8
100	6.8
120	7.8
140	10.6
160	11.8
180	14.9
200	20.4

The results of the oxidation tests at 2200 F. for the coupons coated according to Examples 3 and 4 are shown graphically in FIGURE 6. In this figure, line 24 shows results for Example 3, while line 25 shows results for Example 4.

It will be understood, of course, that the microprobe tracings of FIGURES 3 and 5 show the composition of the outer layer of the coated coupons prior to testing for oxidation resistance.

I claim:

1. In a process for protecting against oxidation at temperatures above about 2000° F. an article comprising a metal matrix selected from the group consisting of (a) at least one metal of atomic number from 27 to 28, inclusive, and (b) alloys in which there is at least 50% by weight of at least one metal of atomic number from 27 to 28, inclusive, alloyed with at least one Group VI–B metal of atomic number below 75, said matrix metal being dispersion-strengthened with a refractory metal oxide having a free energy of formation at 1000° C.

greater than 100 kilocalories per gram atom of oxygen, the steps comprising (1) effecting contact between such article and a uniform mixture comprising, by weight, about 5 to 90% of chromium metal, 0.05 to 5% of a transfer agent selected from the group consisting of (A) iodine and (B) volatile halides of alkali metals, and (C) volatile halides of ammonia, the balance of the mixture being inert material selected from the group consisting of alumina, zirconia, silica and thoria, at least the chromium and inert being particulate and having a size small enough to pass through a 60-mesh sieve (U.S. Standard), (2) heating, while maintaining such contact, in an environment which is inert except for the presence of such transfer agent, at a temperature in the range of about from 2000 to 2450° F., whereby chromium is deposited upon and diffused into said article, and continuing such contact and heating until between 0.005 and 0.100 g./cms.^{2} of chromium has been deposited, and (3) thereafter effecting contact of the product of step (2) with a mixture comprising, by weight, about from .5 to 20% of −60 mesh aluminum metal, and about from .05 to .5% of a transfer agent of the group of step (1), the balance of the mixture being −60 mesh inert of step (1), and (4) heating while maintaining such contact, at a temperature in the range from 1000 to 2300° F. for about from 0.5 to 36 hours at atmospheric pressure.

2. An article comprising (1) a body of a metal matrix selected from the group consisting of (a) at least one metal of atomic number from 27 to 28, inclusive, and (b) alloys in which there is at least 50% by weight of at least one metal of atomic number from 27 to 28, inclusive, alloyed with at least one Group VI–B metal of atomic number below 75, said matrix metal being dispersion-strengthened with a particulate refractory metal oxide having a free energy of formation at 1000° C. greater than 100 kilocalories per gram atom of oxygen, (2) a triplex coating adherently bonded to and integral with said first body, said coating comprising (a) an inner diffusion zone comprising an alloy of said matrix metal with an increasing concentration of chromium up to about 50% by weight in the outwardly direction, (b) a second zone, outward of zone (a), comprising an alloy of said matrix with about 50 to 95% by weight of chromium and up to 10% by weight of aluminum and having said particulate refractory oxide dispersed therein, and (c) an outer zone comprising an alloy of at least one metal of atomic number from 27 to 28, inclusive, containing, by weight, about from 10 to 50% of aluminum and 2 to 30% of chromium.

3. An article comprising (1) a body of nickel metal dispersion-strengthened with particulate thoria, (2) a triplex coating adherently bonded to and integral with said first body, said coating comprising (a) an inner diffusion zone comprising an alloy of nickel with an increasing concentration of chromium up to about 50% by weight in the outwardly direction, (b) a second zone, outward of zone (a), comprising an alloy of nickel with about 50 to 95% by weight of chromium and up to 10% by weight of aluminum and having particulate thoria dispersed therein, and (c) an outer zone comprising an alloy of nickel containing, by weight, about from 10 to 50% of aluminum and 2 to 30% of chromium.

4. An article of claim 3 wherein the body of nickel (1) is dispersion-strengthened with about 2% by volume of particulate thoria.

5. An article comprising (1) a body of alloy matrix metal in which there is at least 50% by weight of nickel, a proportion of molybdenum less than 30% by weight and lesser proportions of zirconium and carbon, said alloy body being dispersion-strengthened with particulate thoria, (2) a triplex coating adherently bonded to and integral with said first body, said coating comprising (a) an inner diffusion zone comprising an alloy of said alloy matrix with an increasing concentration of chromium up to about 50% in the outwardly direction, (b) a second zone, outward of zone (a), comprising an alloy of said matrix with about 50 to 95% by weight of chromium and up to 10% by weight of aluminum, and having particulate thoria dispersed therein, and (c) an outer zone comprising an alloy of nickel containing, by weight, about from 10 to 50% of aluminum and 2 to 30% of chromium.

6. An article comprising (1) a body of alloy matrix metal in which there is at least 50% by weight of nickel and proportions of molybdenum and chromium the sum total being less than 50%, said alloy body being dispersion-strengthened with particulate thoria, (2) a triplex coating adherently bonded to and integral with said first body, said coating comprising (a) an inner diffusion zone comprising an alloy of said matrix metal with an increasing concentration of chromium up to about 50% in the outwardly direction, (b) a second zone, outward of zone (a), comprising an alloy of said alloy matrix with about 50 to 95% by weight of chromium and up to 10% by weight of aluminum, and having particulate thoria dispersed therein, and (c) an outer zone comprising an alloy of nickel containing, by weight, about from 10 to 50% of aluminum and 2 to 30% of chromium.

7. An article comprising (1) a body of alloy matrix metal, the metal content of which is about 80% nickel and 20% chromium by weight, said alloy body being dispersion-strengthened with about 2% by volume of particulate thoria, (2) a triplex coating adherently bonded to and integral with said first body, said coating comprising (a) an inner diffusion zone comprising an alloy of said matrix metal with an increasing concentration of chromium up to about 50% in the outwardly direction, (b) a second zone, outward of zone (a), comprising an alloy of said alloy matrix with about 50 to 95% by weight of chromium and up to 10% by weight of aluminum, and having particulate thoria dispersed therein, and (c) an outer zone comprising an alloy of nickel containing, by weight, about from 10 to 50% of aluminum and 2 to 30% of chromium.

No references cited.

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