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**OXIDATION RESISTANT AND DUCTILE IRON
BASE ALUMINUM ALLOYS**

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This invention relates to metal bodies and products constituted of ferrous based alloys having substantial oxidation resistance and fortified for use in high temperature environments. It is especially directed to ferrous alloy bodies of this character possessed of a core body structure and an integral casing layer in both of which iron and aluminum are the predominant ingredients and which bodies possess sufficient ductility in at least one stage of their constitution to facilitate their cold and/or hot working by conventional procedures. More specifically the invention concerns metal bodies composed of an alloy core essentially consisting of iron and aluminum in solid solution and an external integral casing or facing consisting essentially of compounds of iron and aluminum. The invention also concerns methods for producing ferrous alloy bodies and products of the aforesaid character and includes a welding process and rod utilizing the core body composition of the invention.

Recent developments in the field of gas turbine engines have created a need for alloys capable of withstanding high temperatures and which have sufficient room temperature ductility to facilitate fabrication. Especially desirable are alloys having excellent oxidation resistance under continuous periods of high temperature service and under operations producing thermal shock occasioned by cyclic heating and cooling. As an example of these needs, consider a gas turbine burner liner. It must be made of metal that can be formed to shape and machined. In use it will normally be exposed for substantial periods, to temperatures in the range of about 1600° F. to 2400° F. during operation of the turbine engine. Presently available are only expensive and strategic alloys moderately satisfactory for this application and the problem is therefore to provide a suitable low cost satisfactory alloy structure for this and other applications where one or more of the stated conditions exist.

The substantial heat resistance of certain iron-aluminum alloys with their low content of strategic and expensive raw materials make them attractive. However, experience has indicated that there is a correlation between the oxidation resistance of iron-aluminum alloys and their aluminum content, and between the ductility of iron-aluminum alloys at room temperature and their aluminum content and that a gradual decrease in ductility and increase in heat resistance is normally associated with increased concentration of aluminum in the alloy.

Unfortunately, one of the basic difficulties with iron-aluminum alloys having substantial heat and oxidation resistance is their lack of adequate ductility at room temperature essential to their cold and/or hot working in rolling, forming, bending, and forging operations. Thus our investigations have indicated, for example, that binary iron-aluminum alloys conventionally prepared under slag conditions or in an inert atmosphere and containing about 10% by weight and more of aluminum lack adequate room temperature fabricability i.e., they have less than 5% elongation by standard room temperature tensile testing, are brittle and difficult to process. This is even true at times with respect to iron-aluminum alloy compositions containing between about 8 to 10% by weight of aluminum depending upon processing and heat treatment or when these alloys contain carbon or other alloying ele-

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ments or dissolved gases. In any event unless specially processed, compositions containing aluminum in this range and greater will have insufficient ductility needed for cold working. At least about 10% and in many cases 20% elongation on standard tensile testing specimens at room temperature is required for this purpose. Moreover, it has been found that lack of ductility is an inherent characteristic in ferrous compositions having sufficient aluminum for substantially continuous periods of protection against severe oxidation at elevated temperatures. For instance, at least 8% aluminum is required in the alloy for a temperature of 1800° F. and about 16% aluminum at 2200° F.

Some attempts have been made to reduce the room temperature brittleness of the iron-aluminum alloy products by producing the alloy composition under vacuum melt conditions and this has resulted primarily in some improvement in hot rolling. Efforts to combine with this procedure a reduction in oxygen impurities by adding carbon to the alloy to combine with the oxygen impurities in the melt and give off carbon dioxide or by passing hydrogen through the melt to combine with the oxygen impurities to form water vapor has produced some further improvement in ductility. These procedures are, however, expensive and time consuming. Moreover, cold working is adversely affected by carbon additions especially above 0.03% by weight and where the aluminum content is above about 12% by weight the percentage elongation of the specimens under room temperature tensile tests is generally insufficient for cold working at room temperature, i.e., is below 10% elongation depending upon the specific procedure employed. Thus a 14% iron-aluminum alloy made by vacuum melting procedures will have good oxidation resistance up to 2200° F. for long periods of time but will only have about a 5% elongation at room temperature.

We have made the surprising discovery that the aforesaid problems may be overcome and oxidation and corrosion resistant metal refractory bodies and products of alloys of iron and aluminum useful for high temperature service over long periods of time and having in at least one stage of their making, sufficient elongation at room temperature for hot and cold rolling, may be obtained by a unique process involving initially compounding the body of iron-aluminum alloy using conventional melt procedures with a relatively low content of aluminum, preferably between about 3½% to 8% of aluminum, normally insufficient to render it effectively oxidation resistant above 1800° F. and then coating the exterior of the alloy body with a layer or film of pure or substantially pure metallic aluminum or alloys rich in aluminum, as by spraying, dipping, or other coating procedures, utilizing a suitable flux wherever necessary, and then preferably subjecting the aluminum coated iron-aluminum body in use or preferably prior thereto to a diffusion anneal treatment at a relatively low temperature, in the order of about 1300° F. to 1600° F. for a suitable period, for example, between about one to about three hours.

According to our invention, the aluminum coating provides in combination with the iron-aluminum core body an integral iron-aluminum alloy structure having a facial casing portion or strata high in aluminum which will adapt it for long service exposure at high temperatures and which will have the equivalent oxidation resistance of an iron-aluminum alloy having for instance as much as 16% and more aluminum content. Its outstanding refractory properties at elevated temperatures is evident from oxidation tests made at temperatures ranging from 1800° F. to 2400° F. for periods up to 300 hours without any indication of deleterious damage to the alloy structure or its exposed surface. Moreover, prior to coat-

ing, the iron-aluminum core body will have good room temperature ductility as evident from elongations of 15 to 35% at room temperature under conventional tensile tests and therefore may be readily cold and hot worked. It will, of course, be understood that the coated structures may be slightly worked after coating but will not be nearly as ductile. In fact, they may be brittle, as the coating, depending upon its thickness, will be capable of only limited deformation. The thicker the coating the less deformation is possible. It is therefore preferred that any forming, machining or other operations be performed prior to coating so that the full benefit thereof may be obtained in subsequent use.

The exact nature of what occurs in the coated structure to produce the foregoing excellent results is not exactly known, but some idea may be had from a comparison of what is believed to occur upon aluminum coating and heat treating an ordinary iron or plain carbon steel core with a similarly coated core of iron-aluminum alloy. In the first case the pure aluminum and compounds of iron and aluminum such as FeAl_3 , FeAl , and Fe_3Al believed to constitute the composition of the outer layer are believed upon heating to diffuse inwardly to completely combine, for all practical purposes, with the iron core material to form solid solutions of aluminum and iron and produce surface areas of aluminum oxide that will slag away with iron oxide after short periods of exposure at temperatures above 1800° F. Stated otherwise, rapid oxidation occurs. In the second case where in accordance with the present invention, the core is an iron-aluminum alloy, preferably containing at least about 3½% by weight of aluminum in solid solution with the iron of this core and the aluminum is in sufficient amount that it tends to resist and retard the migration of the pure aluminum and iron-aluminum compounds of the surface coating into the body to form solid solutions of iron and aluminum. These surface compounds which contain as much as 50% (atomic weight) and more aluminum therefore remain to protect the structure from rapid oxidation at high temperatures. Moreover, after these compounds are all used up by oxidation over extended exposures, there will still be at the surface the solid solutions of iron and aluminum of the core structure or that formed following coating and although these solid solutions are not believed as resistant to oxidation as the aluminum compounds they will nevertheless provide considerable protection.

In some instances as where severe oxidation conditions at high temperatures are anticipated, our invention may utilize a core body made by conventional melt procedures using greater amounts of aluminum than will provide ductility but preferably using the vacuum melt procedures referred to above in order to start with a core material of ductile character higher in aluminum than conventionally possible, in either event to obtain by means of the iron-aluminum surface compounds even greater oxidation resistance than described above for alloys having such percentages of aluminum. Furthermore, some of the novel benefits of our invention may also be obtained by recoating with aluminum and heat treating a core of iron previously coated with aluminum and heat treated, so as to provide in effect an under surface of a solid solution of iron and aluminum as a surface repellent barrier to the aluminum compounds produced by the second coating.

Accordingly, it is the principal object of our invention to provide aluminum coated ferrous based aluminum alloy bodies characterized by oxidation resistance at relatively high temperatures in the order of 1600° F. to 2400° F. and that have sufficient room temperature ductility in at least one stage of their making to facilitate hot and cold fabrication by conventional procedures.

A related object is to provide a ferrous body comprising pure iron, carbon steel and the like having a surface strata comprising iron and aluminum in solid solution

overlaid with compounds of iron and aluminum to render the body resistant to oxidation at high temperatures.

A specific object is to provide a metal structure predominantly of iron and aluminum and composed of an iron based alloy body possessed of room temperature ductility and containing relatively small amounts preferably between about 3½ to about 8% by weight of aluminum which body has a surface coating of aluminum diffused therewith to provide with said body a structure having excellent resistance to substantial oxidation and disintegration at elevated temperatures.

A further specific object is to provide an iron-aluminum alloy body as in the preceding object wherein said body contains between about 8 to about 12% aluminum incorporated therein by vacuum melting procedures with or without removal of oxygen impurities.

A further specific object is to provide iron-aluminum alloy bodies capable of substantial oxidation resistance and hot working at elevated temperatures between about 1600° F. and 2400° F. comprising a workable iron-aluminum alloy core containing less than about 16% aluminum but more than about 3% thereof and an exterior iron-aluminum stratum or layer containing above about 20% aluminum by weight and in concentration greater than that of the core.

Other objects and advantages of our invention will become more evident from the following description.

According to the present invention, an iron-aluminum alloy body that is of ductile character and that has an elongation of at least about 10% at room temperature may be formed by conventional melting methods so as to preferably contain between about 3½% to 6% aluminum by weight, and even up to 8% by weight where proper precautions are taken in processing. If made by vacuum melting procedures the aluminum content may be up to about 12% by weight. The alloy body in this ductile condition is then preferably cold or hot worked as desired to predetermined shape and size and machined as needed. It is then coated with an aluminum base material which may be pure metallic aluminum or an aluminum alloy rich in aluminum. Any conventional procedure with or without fluxing may be employed for producing this coating but best results are found to be obtained by employing hot dipping procedures in which the iron-aluminum alloy body to be coated is immersed in a bath of molten aluminum or aluminum alloy at a predetermined temperature for a predetermined length of time sufficient to effect a satisfactory coating thereof.

The aluminum coating treatment may be performed continuously or by means of a batch-type process. The temperature of the bath of molten aluminum or aluminum alloy is subject to considerable variation, a range of 1300° F. to 1500° F. having been found to produce satisfactory results. The period of treatment in the molten bath may vary from a few seconds to an hour depending upon the size of the body or core being treated. The thickness of aluminum coating to be obtained on the core body is not too critical and is preferably in the order of one to ten thousandths of an inch.

Following coating, the treated alloy body is preferably heat treated. In most cases it will be found that a temperature in the order of about 1500° F. for a period of about two hours will suffice. This treatment assures the diffusion of the free aluminum of the coating into the surface of the core to form with migrating iron therein further high melting point iron-aluminum compounds believed to be responsible for the refractory character of the aluminized iron-aluminum alloy body. The heat treatment is believed to increase the case depth or thickness of the protective layer sufficiently to materially improve the oxidation resistance of the body but the depth or thickness is not made so great that the concentration of aluminum in the case or layer is diluted enough to permit substantial impairment of the oxidation resistance of the body at high temperatures. It will be understood

that the heat treatment is not limited to the time and temperature given but may be subject to considerable variation in temperature and time. For example if the conditions are right it may take place in actual use, although such is not recommended if the temperature is above 1800° F. as the total oxidation resistance of the body is reduced thereby. The aluminized iron-aluminum alloy body is found to withstand severe oxidation conditions at temperatures above 1600° F. and even as high as 2400° F. and to an extent not possible with aluminum coated plain carbon steels. As previously stated, the exact reason for the improved or beneficial effect of the diffused aluminum coating upon the iron-aluminum base alloy is not fully understood. In addition to reasons already expressed, it is believed that the coating is responsible for producing substantially stable iron-aluminum compounds of high aluminum content and consequently of higher refractory character at the surface. The greater oxidation resistance may also possibly be explained by the fact that the aluminum concentration gradient between the core and the coating is at a much lower value than in the case of aluminized steel and consequently the rate of decomposition of the iron-aluminum compound at the surface and diffusion of the aluminum from the surface at elevated temperatures is appreciably reduced.

Although as pointed out above, small additions of aluminum to substantially pure ferrous bodies or ferrous base alloy bodies appear to improve their oxidation resistance in the aluminized condition, a minimum level of aluminum, over about 3% by weight alloyed with the ferrous base material is required to develop a refractory alloy resistant to oxidation at temperatures up to about 2400° F. We have found for example by experimentation that an iron-aluminum alloy body containing about 3½% by weight of aluminum and which is aluminum coated and heat treated, has a life in the order of about 50 hours when heated in air at 2200° F. Moreover, the oxidation resistance of such an aluminized body wherein the alloy body contains about 4¼% was found to be considerably better than the 3½% material, but one containing about 5¼% aluminum exposed to the same conditions as the 3½% alloy was not damaged at all after a period of more than 300 hours duration.

In the preparation of the iron-aluminum core or body, it is preferred that any carbon alloying content of the alloy be kept as low as possible because it is found that carbon decreases the oxidation resistance of aluminized iron-aluminum alloys. We have also found that a decrease in the room temperature ductility of the iron-aluminum alloy results from an increase of the carbon content above the range of about 0.03% to 0.05%. In general, the effect of alloying additions, other than aluminum to the iron, on the oxidation resistance of iron-aluminum alloy bodies aluminized as described above and upon their other physical properties seems to be that at relatively low levels of alloying content with elements other than aluminum there is only a slight decrease or no appreciable effect on the oxidation resistance of the aluminized iron-aluminum base alloy but at high levels of such alloying with elements other than aluminum the resistance to oxidation appears to be reduced appreciably. The following table presents preferred ranges of alloying additions other than aluminum for the compositions of the invention. It will be understood, however, that the invention is not limited thereto:

	Percent by weight
Carbon -----	as low as possible up to 0.5
Silicon -----	0-5
Titanium -----	0-5
Chromium -----	0-25
Manganese -----	0-30
Nickel -----	0-30
Columbium -----	0-7
Molybdenum -----	0-10
Tungsten -----	0-10

Percent by weight

Vanadium -----	0-10
Cobalt -----	0-20
Copper -----	0-3
Zirconium -----	0-5

Not only does the aluminum alloying of the ferrous body improve its oxidation and scale resistance in the aluminized condition, but such also protects welds in the body from destruction by substantial oxidation during exposure at high temperatures. Deterioration of the weld has heretofore been experienced after 100 hours of exposure with steel structures welded with conventional welding rods or by simple "Heliarc" joining and then coated with aluminum. Where steel pieces to be welded and aluminum dipped were welded using a welding rod made from the iron-aluminum compositions of our invention, for instance an iron-aluminum alloy containing about 6% aluminum, as the electrode, the use of such rod has successfully prevented oxidation of the welded area. An aluminum coated welded area of this kind when exposed to oxidation at a temperature of 1700° F. showed no oxidation after 300 hours whereas a weld made with stainless steel and similarly heated for only 240 hours showed very definite scale and oxidation and showed the presence of black oxide after only 100 hours of exposure. The aluminum content of the welding rod alloy composition will be at least about 3% by weight preferably at least about 6% by weight and the aluminum coated welded area will be preferably heat treated as described above with regard to the composition products made by this invention.

A fuller understanding of the invention and its further objects and advantages will be had from the following examples of specific metal structures and of typical processes by which they may be produced. Such examples are intended only for illustration of the invention and not as a limitation upon its scope. Wherever in the following examples reference is made to tensile testing such tests were made in accordance with standard ASTM practice and at room temperature.

Example I

An alloy composition of iron and aluminum was prepared under an argon atmosphere by melting, by induction heating in a magnesia crucible, 1780 grams of electrolytic iron after which 120 grams of commercial 2S aluminum was added to the molten iron and stirred thoroughly therein. The molten alloy containing approximately 6% by weight of aluminum was then poured into an investment mold assembly comprising several tensile test bars and one ¾" round bar.

The ¾" alloy bar was then sectioned into slugs and machined to 0.70" diameter and 0.250" long. The machined slugs were then degreased in a trichloroethylene bath and coated with any conventional flux such as "Alcoa" No. 33 flux and preferably a flux such as described in the copending application of Walter E. Jominy et al. Serial No. 344,190, filed March 23, 1953. The slugs were then aluminum-coated by hot dipping them into a bath of commercial 2S aluminum maintained at a temperature of 1350° F. and held in the bath for a period of two minutes after which they were removed. The coated slugs were then diffusion annealed at a temperature of 1500° F. for two hours.

Oxidation tests were carried out on the samples in still air in a furnace held at a predetermined temperature. Duplicate samples were tested at temperatures ranging from 1800° F. to 2500° F. Weight change measurements as well as visual observations were made at regular intervals during the testing. From this testing and observations it was apparent that the coated alloy would incur no damage whatever in oxidation tests when the material was tested at 1800° F. for 200 hours, at 2000° F. for 300 hours, and at 2400° F. for 240 hours. The mechanical properties of the alloy were measured at room

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temperature and at 1350° F. Conventional tensile tests at room temperature prior to coating indicated that the ductility of the alloy was good and averaged 27% elongation in the samples. The alloy made herein contained a nominal 6% aluminum by weight and 5.65% aluminum by analysis.

Example II

An alloy of iron and aluminum was prepared from commercial grade materials employing the same procedure as described with respect to Example I using in this instance SAE 1010 steel as the base material and 2S aluminum. The alloy made in accordance with this example upon testing showed substantial oxidation resistance but was somewhat lower than that for the alloy of Example I at extremely high temperatures. Moreover this alloy was relatively brittle in the cast condition at room temperature and its elongation was 0.5%.

Example III

An alloy was prepared as in Example No. I using Armco iron as the base material. Upon testing this material prior to coating it was found to be very ductile. It had an elongation of between 16 to 20% by room temperature tensile testing. Moreover after aluminum coating this alloy was found to withstand severe oxidation conditions at elevated temperatures and was substantially equal to the alloy of Example I in this characteristic.

Example IV

An iron base aluminum alloy was prepared in accordance with the procedure of Example I using the same base and alloying materials but employing 1% of aluminum by weight. The oxidation resistance of this alloy structure was good for 53 hours at 2000° F. and 25 hours at 2200° F. The material was very ductile.

Example V

An alloy structure was prepared in accordance with the procedure of Example I using the same base and alloying materials but wherein the percentage by weight of aluminum was 2%. The oxidation resistance of this structure was good for 95 hours at 2000° F., 25 hours at 2200° F. and 20 hours at 2400° F. The material had an elongation of 35 to 40% under short time tensile testing at room temperature.

Example VI

An alloy structure was prepared as in Example I differing in using 3% aluminum. The oxidation resistance of this structure was good for 95 hours at 2000° F., 25 hours at 2200° F., and 20 hours at 2400° F. The material had an elongation of 40 to 42% by tensile testing at room temperature prior to coating.

Example VII

An alloy structure was prepared in accordance with Example No. I employing 4% aluminum. The oxidation resistance of this material was good for 95 hours at 2000° F., 50 hours at 2200° F., and 20 hours at 2400° F. The material had an elongation of 33 to 35% by tensile testing at room temperature prior to coating.

Example VIII

An alloy structure was prepared in accordance with Example No. I using 5% aluminum by weight. Oxidation tests indicated no damage to the samples after 225 hours at 2000° F. The material had an elongation of 28 to 30% by tensile testing at room temperature prior to coating.

Example IX

An alloy structure was prepared in accordance with the procedure of Example I using 8% aluminum. On oxidation testing the material exhibited no damage at 2000° F. after 300 hours, at 2200° F. after 240 hours, at 2400°

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F. after 265 hours, and 2500° F. after 100 hours. The material had an elongation of between 5 to 20% by tensile tests at room temperature.

Example X

An alloy structure was prepared in accordance with the procedure of Example No. I using 10% aluminum. On oxidation testing this alloy structure exhibited no damage upon testing at 2200° F. for 240 hours, at 2400° F. after 265 hours, and at 2500° F. after 100 hours. The material had an elongation of between 1 to 3% by tensile testing at room temperature prior to coating.

Example XI

An alloy structure was made in accordance with the procedure of Example I using 14% aluminum. Upon oxidation testing the structure showed no damage after testing at 2400° F. for 265 hours and at 2500° F. after 100 hours. The structure had an elongation of less than 1% by tensile testing at room temperature prior to coating.

Example XII

An alloy structure as described in Example X was made by vacuum melt procedures to obtain greater ductility at room temperature.

Example XIII

5640 grams of Armco iron was melted under a $\text{CaCO}_3/\text{CaF}_2$, 1:1 slag by induction heating. 360 grams of 2S aluminum was fed through the slag and the alloy was then poured in a shell mold to form a 3" diameter ingot. The ingot which contained about 6% aluminum by weight was then forged at 1800° F. down to $\frac{3}{4}$ " slab. The slab was then further reduced down to a sheet of a thickness of 0.080" by hot and then cold rolling. This sheet material was then used in the fabrication of gas burner liners, the joint of the liners being welded by "Heliarc" welding using welding rods made from the parent metal forming the sheet as a filler. The gas burner liners were cold formed at room temperature prior to coating by conventional methods. Ample ductility was present for the operation. The liners were then aluminum coated as described in Example No. I and then both liner and weld subjected to oxidation testing at temperatures up to 2400° F. The weld was tested, for example, for 325 hours at 2000° F. without any sign of damage. This was also true under more severe oxidizing conditions. The liner was also tested in actual use in a turbine engine and after many hours of operation showed no deterioration from oxidation at the high temperature prevailing.

It is obvious that many variations may be made in the products and processes of this invention without departing from the spirit and scope thereof as defined in the appended claims.

We claim:

1. A ferrous base metal product capable of substantial resistance to oxidation and scaling upon exposure to high temperatures in the order of 1600° F. to 2400° F. comprising a metallic inner body consisting essentially of iron and aluminum in solid solution, said inner body having a substantially equal aluminum concentration throughout in amount between at least 3% and not more than 12% by weight of the body and said inner body having thereon a metallic layer consisting essentially of iron and aluminum compounds whose aluminum content is at least about 20% by weight.

2. A ferrous base product as claimed in claim 1 wherein said aluminum concentration in said body is between $3\frac{1}{2}$ % to 8%.

3. A ferrous base product as claimed in claim 1 wherein said aluminum concentration in said body is between $5\frac{1}{4}$ % to 8%.

4. A ferrous base metal product as claimed in claim 1 wherein said inner body includes in solid solution with the iron and aluminum other ingredients selected from

the group consisting of the following elements and mixtures thereof and within the limits stated:

	Percent by weight
Carbon -----	0-0.5
Silicon -----	0-5
Titanium -----	0-5
Chromium -----	0-25
Manganese -----	0-30
Nickel -----	0-30
Columbium -----	0-7
Molybdenum -----	0-10
Tungsten -----	0-10
Vanadium -----	0-10
Cobalt -----	0-20
Copper -----	0-3
Zirconium -----	0-5

5. A ferrous base metal product capable of substantial resistance to oxidation and scaling upon exposure to high temperatures in the order of 1600° F. to 2400° F. comprising an inner cold workable body possessing at least about 10% elongation by standard tensile testing at room temperature and consisting essentially of iron and aluminum in solid solution, said inner body having a substantially equal aluminum concentration through-

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out in amount between about 5¼% to 8% by weight of said body and said body having a surrounding protective layer integral therewith consisting essentially of aluminum and iron-aluminum compounds in which the aluminum concentration is at least 20% and more by weight.

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