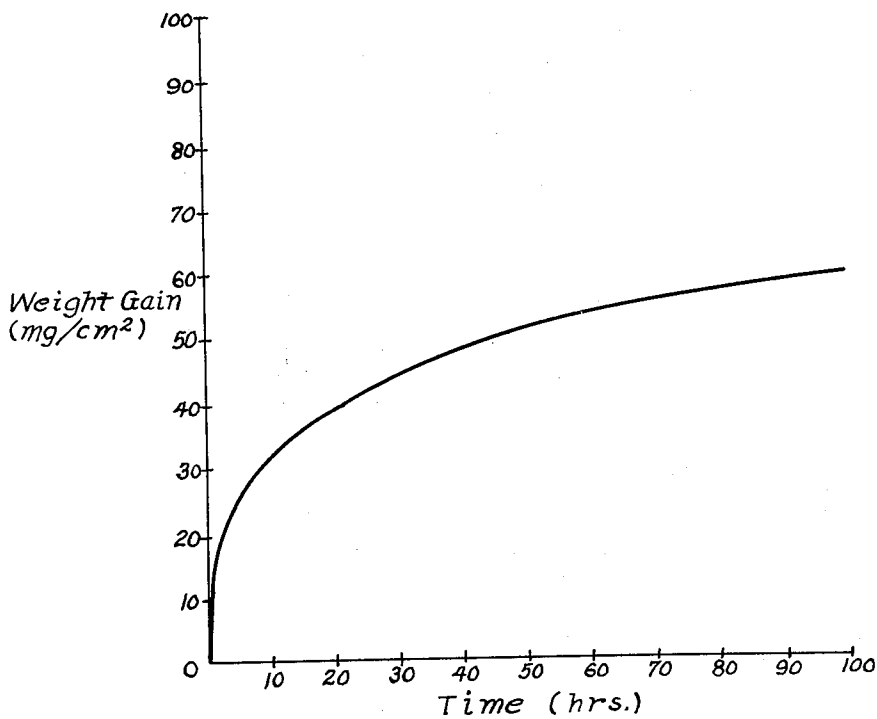


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NIOBIUM-ZIRCONIUM BASE ALLOY

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*Plot of Weight Gain vs. Time for the oxidation
in still air of alloy (45%Nb-50%Zr-5%Ti) at 1000°C.*

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NIOBIUM-ZIRCONIUM BASE ALLOY

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The present invention relates generally to high temperature and corrosion resistant metallic alloys, and more specifically to an improved niobium-zirconium base alloy having these desirable properties.

In the past, various niobium base alloys have been proposed, but by and large, such alloys exhibit relatively poor high temperature oxidation resistance, due to the relatively high percentage of niobium present therein and/or the inclusion of certain other metals which make the resultant alloys relatively brittle and subject to progressive and continuous oxidation.

It is, therefore, the primary object of the present invention to provide an improved high strength, high temperature oxidation-resistant alloy which consists essentially of a homogeneous mixture of niobium, zirconium and titanium.

It is a further object of this invention to provide a niobium-zirconium base alloy which exhibits exceptional oxidation resistance at high temperature, and one which is characterized by its ability to form a tenacious, uniform and stable oxidized protective coating upon its normally exposed surfaces, which protective coating represents an extremely low percentage of the overall weight of the alloy and at the same time prevents further and progressive oxidation of the alloy.

Another object of the present invention is to provide a high temperature oxidation-resistant alloy which is characterized by a relatively low thermal neutron cross-section, thus making the alloy particularly suited for use in high temperature nuclear applications.

A further object of this invention is to provide an alloy which, due to its high temperature and corrosion resistance, its good strength properties and its unusual surface hardness, may be used as a base material for parts of gas turbines, jet engines, and for parts of numerous other equipment designed to operate at relatively high temperatures, and requiring good strength and hardness characteristics.

For a further and more complete understanding of the present invention, reference is made to the following detailed description and the accompanying drawing, wherein the single figure is a graph disclosing the oxidation rate of a typical alloy formed in accordance with the present invention and illustrating particularly how the rate of high temperature oxidation of the present alloys decreases over a relatively short period of time to a point where a substantially stable oxidized condition exists.

Alloys formed in accordance with this invention comprise compositions containing from 39% to 60% by weight of niobium, from 60% to 39% by weight of zirconium, and from 1% to 6% by weight of titanium.

For maximum efficiency, the percentage ranges of the various component metals which comprise the present alloys are preferably from 45% to 57% by weight of niobium, 52% to 40% by weight of zirconium, and 1% to 3% by weight of titanium.

Alloys of the present invention may be prepared uti-

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lizing conventional and well known equipment and metal melting and remelting techniques. For example, alloys of the present invention may be prepared in an electrical arc melting furnace having a water-cooled copper crucible, such as is described in detail in the publication "Transactions of the Electrochemical Society," vol. 78, 1940, article by W. Kroll, pp. 35-47. It is also possible to prepare the present alloys using consumable arc electrode furnaces, or by the electrical induction heating of the charge in a suitable crucible or mold. In all cases, however, it is necessary to protect the molten metals against contamination by oxygen, nitrogen and other more or less reactive gases. Toward this end a protective and controlled atmosphere composed of an inert gas or gases, such as argon, helium, etc., is maintained in and around the crucible or mold during the melting and remelting of the metal constituents of the alloys. The use of inert gases during the melting of metals is well known in the art.

Specific examples, which are illustrative of the preparation of high temperature oxidation-resistant alloys of the present invention, are as follows:

Example 1

An initial charge consisting of 46% by weight of niobium, 51% by weight of zirconium and 3% by weight of titanium was prepared by cutting the individual metals into relatively small size pieces or chunks and introducing the pieces into a water-cooled copper crucible of an electrical arc melting furnace. This charge was then melted and the initial melt was permitted to solidify. The ingot produced by the initial melting was then inverted in the crucible, remelted and resolidified. The alternate remelting, solidifying and inverting of the alloy was carried out three times to thus homogenize the alloy. The melted and remelted alloy was then cast into a 5 gram button of hemispherical shape using a hemispherical mold which was machined into the copper hearth of the furnace. During the melting, remelting and casting of the specimen, an inert atmosphere of argon gas was maintained about the alloy to prevent contamination thereof.

The cast alloy was then removed from the mold, cold rolled 25%, and then machined into a rectangular prism to provide a test specimen. This test specimen was suspended by a platinum wire from one pan of an analytical scale balance mounted above a vertical tube furnace having a silicon carbide heating element, which furnace is commonly known in the art as a vertical tube Globar furnace. In this arrangement, the test specimen was suspended in the heating zone of the furnace and was exposed for 100 hours, to a temperature of 1000° C., in preheated air flowing through the furnace at the rate of 4 cubic feet per minute. By this arrangement the specimen could be weighed while remaining at the aforementioned temperature within the furnace. At the end of 100 hours at this temperature, the specimen gained 57.0 milligrams per square centimeter of surface area. This amounted to a total weight gain of 1.2%. An examination of the outer surface of this specimen revealed a very dense, adherent and substantially stable oxide coating over the entire specimen.

By way of comparison, a control test specimen formed from pure niobium along was tested under the same conditions, and was found to gain 40 milligrams per square centimeter of surface area for "each one hour" period at 1000° C. until the niobium specimen was completely oxidized.

Example 2

Employing the same melting and remelting procedures and equipment as described in the foregoing Example 1,

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a second alloy containing 45% by weight of niobium, 50% by weight of zirconium and 5% by weight of titanium was prepared. A specimen of this alloy was heated to a temperature of 1000° C. and maintained at such temperature in still air for a period of 100 hours, during which time the specimen was periodically check-weighed to determine weight gain, due to oxidation. The results of this operation are shown graphically in the accompanying drawing, from which it will be noted that the alloy underwent a very rapid initial weight gain during the first two or three hours at temperature, but thereafter the rate of weight gain of the alloy progressively decreased with increasing time to a point that the rate of weight gain after 100 hours at temperature was, for all intent and purposes, negligible. This progressive decrease in the rate of high temperature oxidation is typical of alloys of the present invention and illustrates the ability of the present alloys to form a stable, dense, adherent and protective oxidized coating or film upon their outer surfaces which serves to minimize further and progressive oxidation and deterioration.

Example 3

Using the same melting and remelting procedure and equipment as described in Example 1, a third alloy containing 49% by weight of niobium, 50% by weight of zirconium and 1% by weight of titanium was prepared. Following the initial melting and the alternate solidifying, inverting and remelting (3 times), a one gram sample was cut from the resultant ingot. This one gram sample was remelted and then poured, using an argon atmosphere, into a spherical-shaped mold machined into the copper hearth of the furnace. The resultant spherical sample was placed upon a porcelain plate and then introduced into a Globar muffle furnace where it was heated to a temperature of 1000° C. and exposed to air for a period of seven hours. At the end of seven hours, the spherical test sample was removed from the furnace, allowed to cool to room temperature and was check weighed. An inspection of the exterior surface of the sample revealed an extremely dense and tenaciously adherent oxide scale substantially covering the spherical sample.

The spherical sample was then replaced in the furnace and reheated to 1000° C. Over a total period of 85 hours at a temperature of 1000° C., the sample was periodically removed from the furnace, cooled, check weighed and replaced in the furnace a total of five times. Following this procedure the test sample was finally removed from the furnace, check weighed and examined as to its surface properties. The total weight gain after 85 hours at the above temperature was 61 milligrams per square centimeter of surface area, and the specimen was found to contain a very dense and adherent oxide film or surface coating.

In contrast, a test specimen formed of pure niobium alone and tested under the same conditions, revealed a considerably higher and progressive rate of oxidation, and the oxide scale formed on the pure niobium specimen was almost completely non-adherent and readily spalled off of the specimen each time the same was cooled.

Example 4

Following the same procedure as described in Example 1, an alloy containing 47% by weight of niobium, 51% by weight of zirconium and 2% by weight of titanium was prepared. A sample of the resultant alloy was heated in air at a temperature of 1000° C. for ten hours, then cooled to room temperature and weighed. The total weight gain of the sample was 34 milligrams per square centimeter of exposed surface, and the exterior surface of the sample contained a dense, adherent oxidized film or coating.

Example 5

Again using the same procedure as specified in Example 1, another alloy containing 52% by weight of

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niobium, 45% by weight of zirconium and 3% by weight of titanium was prepared. This alloy, after being heated to 1000° C. for ten hours in air, was check weighed and revealed a weight gain of 38 milligrams per square centimeter of surface area, and a dense and adherent oxidized surface coating.

Example 6

Following the same melting and remelting procedures as described in Example 1, still another alloy containing 57% by weight of niobium, 40% by weight of zirconium and 3% by weight of titanium was prepared. A sample of this alloy, after being heated to 1000° C. for ten hours in air, revealed a weight gain of 40 milligrams per square centimeter of surface area, and a dense and adherent oxidized surface coating.

Example 7

Using the same procedure as specified in Example 1, another alloy containing 41% by weight of niobium, 56% by weight of zirconium and 3% by weight of titanium was prepared. This alloy, in the form of a rectangular prism, was heated in flowing air at 1000° C. for ten hours and revealed a weight gain of only 28 milligrams per square centimeter of surface area. After twenty hours at 1000° C. the same specimen showed a total weight gain of 34 milligrams per square centimeter of surface area.

In the foregoing specific examples of the preparation of the present alloys, the component elements or metals used therein were of the following purity:

	Percent by weight
Niobium bar	99.72
Zirconium bar	99.99
Titanium bar	99.9+

The minor percentage of impurities normally present in the commercially pure forms of the individual constituent metals have been found not to adversely affect the desirable properties of the present alloys. However, actual tests have shown that when attempts were made to replace the titanium constituent with other metals, such as nickel, chromium, molybdenum, iron, or cobalt, the substitute metals were either insoluble or else resulted in the formation of alloys which were too brittle for any practical usage and which did not possess oxidation resistance equal to those alloys containing titanium.

Further actual tests have shown that the use of niobium and zirconium as the sole constituents of the alloy results in an inferior oxidized surface coating and one which easily flakes from the surface of the alloy, thus permitting undesirable continued and/or progressive oxidation. Thus, the addition of titanium in the range of 1-6% by weight of the alloy results in an extremely dense, adherent and substantially stable oxidized surface coating, which prevents or minimizes continued or progressive oxidation of the alloy.

Through actual experiments and replicate tests, it has been found that mixtures containing the three constituent metals, niobium, zirconium and titanium, but in proportions outside of the ranges of 39-60% by weight niobium, 39-60% by weight zirconium and 1-6% by weight titanium, result in alloys which are susceptible to a materially higher rate of oxidation and which are characterized by inferior, largely non-adherent oxide surface coatings.

Thus, by controlling the proportions of the three constituent metals within the ranges specified, it has been found that the amount of oxidation, particularly at high temperatures of the order of 1000-1200° C., is minimal and that the oxide layer (niobium and zirconium oxides) formed on the outer surfaces of the alloy is of a dense, hard and tenacious character, such as will serve to prevent continued and progressive oxidation of the alloy. In this regard, it has been found that the major propor-

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tion of the surface oxidation of the present alloy occurs in the first few hours when the alloy is exposed to high temperature oxidation conditions, and that thereafter the rate of oxidation decreases progressively until after approximately 100 hours of exposure there is substantially no further oxidation.

In view of the foregoing, it will be seen that the present invention provides an improved niobium-zirconium base alloy which is subject to a minimal amount of oxidation at relatively high temperatures and which is capable of forming a stable, dense and tenaciously adherent protective coating upon its outer surfaces which inhibits further and progressive oxidation or corrosion.

Thus, alloys of the present invention are particularly useful in the formation of various parts or pieces of equipment to be used in relatively high temperature surroundings, such as in gas turbines, jet engines, nuclear reactors, furnaces or the like.

Having thus described this invention, what is claimed is:

1. An oxidation-resistant alloy consisting, apart from impurities, of niobium, zirconium and titanium in the approximate percentages by weight of 39-60% niobium, 39-60% zirconium and 1-6% titanium.

2. An alloy consisting, apart from impurities, of 45 to 57% by weight of niobium, 52 to 40% by weight of

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zirconium, and 1 to 3% by weight of titanium, said alloy being resistant to progressive oxidation at temperatures of the order of 1000° to 1200° C.

3. A niobium-zirconium base alloy characterized by its ability to form on the exposed surfaces thereof a tenacious, uniform and substantially stable oxidized protective coating and consisting, apart from impurities, of approximately 39 to 60% by weight of niobium, 39 to 60% by weight of zirconium and 1 to 6% by weight of titanium.

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