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OXIDATION RESISTANT NIOBIUM

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The present invention relates to oxidation resistant niobium and more particularly, to a method of making a niobium article oxidation resistant at elevated temperatures.

Niobium possesses basic properties which make it a favorable material for use in equipment and components designed to operate at high temperatures. It also possesses properties which make it a favorable material for use in nuclear applications. These properties include: (a) moderate thermal neutron cross section, (b) low coefficient of thermal expansion, (c) negligible volatility, (d) intermediate density, (e) low diffusion rates of foreign atoms, (f) elevated temperature strength, (g) thermal shock resistance, (h) availability, and (i) fabricability. The full utilization of these properties has not yet occurred because an adequate means for imparting oxidation resistance to niobium for service in oxidizing atmospheres at elevated temperatures has not been developed.

It is an object of the present invention to make the extremely favorable combination of basic properties possessed by niobium more readily available by providing a method of protecting the niobium material from destructive oxidation at elevated temperatures.

A further object of this invention is to provide a process whereby niobium may be made oxidation resistant in oxidizing atmospheres at temperatures in the neighborhood of 2500° F.

Other objects will be apparent from the description of the present invention which follows.

In accordance with the present invention, it has been found that oxidation resistance can be provided niobium by infiltrating a porous structure of niobium with a low melting point aluminum-chromium-silicon alloy. The resultant composite structure retains a continuous ductile phase of niobium, preserving the favorable properties of niobium, and exhibits oxidation resistance not limited to the surface of the material, but existent to a considerable distance beneath the surface.

The porous structure of niobium required for the process of this invention must be carefully prepared. An acceptable structure containing pores of preferred size may be prepared by using unalloyed niobium powder of —325 mesh. The powder must be of a high order of purity. An excess of impurities may cause excessive diffusion of coating constituents into the niobium particles, thereby destroying their integrity.

The niobium powder may be formed into the desired configuration by means of slip casting techniques. Metal powder slips have been prepared by slowly adding —325 mesh niobium powder to a mixture of sodium alginate and hot water. These materials are well mixed using a blender. After blending, the material should be protected from the air by storing in a suitable container. The niobium slip material, having the consistency of heavy oil, may then be cast into shape using plaster molds. Within approximately 24 hours enough moisture from the slip is removed by absorption into the plaster to permit handling. The castings may be removed from the mold and sintered at 3650° F. for one hour in a vacuum of at least 0.1 micron. The resultant porous niobium material is then ready for impregnation.

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A low melting point alloy is used to impregnate the porous niobium structure. Broadly, a suitable low melting alloy contains, by weight, 5% to 20% chromium, 0 to 20% silicon, 0 to 10% titanium, and the balance aluminum. Preferably, the alloy contains, by weight, 10% chromium, 3% silicon, and the balance aluminum. This molten alloy will freely flow throughout the porous niobium structure to form a stable, refractory, oxidation resistant structure. Oxidation resistance of the impregnated niobium structure can be enhanced by the addition of 3% to 5% by weight, preferably 5% by weight, of titanium. A complex spinel type oxide is produced on the surface of the niobium by the addition and reaction of the aluminum, chromium, and titanium constituents. Silicon assists in stabilizing the coefficient of expansion between the final ceramic oxide and the niobium metal skeleton, but an excess will also lower the oxidation resistance of the niobium. Preparation of the alloy for the impregnation comprises melting the solution in an alumina crucible using a global furnace capable of heating the alloy solution to 2150° F. The aluminum component is melted initially, and to this melt electrolytic flakes of chromium are added. If silicon and titanium are included, chunk silicon is added first and then crystal bar titanium. Heating is continued to ensure that all the elements will become dissolved in the melt. Approximately ½ to 1 inches of flux is maintained on the surface of the melt at all times to prevent contamination.

After all the metal constituents have formed a homogeneous melt, the porous niobium material is immersed into the molten solution at 2150° F. for about 15 seconds. When the material is removed, the excess liquid metal may be removed by vigorously shaking. This immersion treatment produces only a partial penetration of the porous niobium structure, and additional treatment, similar to zone-refining, is necessary to produce a completely impregnated article.

The zone melting technique may be performed in standard apparatus capable of holding a vacuum. Illustrations of suitable apparatus may be found in Zone Melting by Pfann, John Wiley & Sons, Inc., p. 75. Usually, the partially impregnated niobium article is placed in a hollow cylindrical graphite susceptor which has been outgassed by heating in vacuum to 4000° F. for a period of 2 hours. The article and graphite susceptor are in turn positioned within a quartz tube and the entire system is evacuated to at least 0.1 micron of Hg. The quartz tube is physically coupled to a mechanical traversing mechanism which automatically moves the specimen and container through an induction heating coil at a prescribed rate.

The rate at which the specimen passes through the heating coil and the temperature of the localized portion of the specimen being heated determines the extent of infiltration and the success of the coating process. In any one instance there are three zones of reaction closely associated with the position of the heating coil. In the center of the coil is the zone of highest temperature. Here the low melting point oxidation resistant alloy previously concentrated at the surface as a result of the dipping operation is superheated and flows freely in a radial direction into the niobium structure. The high temperature in this zone causes partial reaction of the constituents of the alloy with the niobium particles. In the zone adjacent the approaching coil, the excess liquid alloy is pushed away from the highest temperature area. On the already heated and partially reacted surfaces, excess solution is evaporated by the high vacuum and the high vapor pressures of aluminum and chromium.

After running over the length of the specimen, the metallurgical result is a continuous porous network of ductile niobium with surfaces coated with an extremely

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thin layer of high melting point oxidation resistant alloy. The protective surface layers consist primarily of high melting point niobium-aluminum intermetallic compounds which are extremely oxidation resistant when proper amounts of chromium, silicon, and preferable titanium, are present.

The ductility and workability of the resultant niobium structure are such that the material may be further densified by reducing its cross section by swaging at room temperature or by conventional wrought metal processing techniques. The final structure is a dense composite of niobium with a minor phase of refractory oxidation resistant alloy.

Extensive oxidation testing of these composites has been carried out. Samples prepared according to the method disclosed above have successfully operated in air for periods in excess of 1000 hours at 2500° F. and with more than 50 thermocycles being imposed at a rate of approximately 1000° F. per minute between test temperature and room temperature.

The decided improvement in the oxidation resistance of niobium at evaluated temperatures makes niobium metal treated by the process herein disclosed extremely attractive for use in nuclear reactors, high temperature turbines, and rocket and missile construction.

We claim:

1. A composite oxidation resistant refractory article comprising a porous niobium skeleton having a low melting aluminum, chromium, silicon, and titanium alloy dispersed in said skeleton.

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2. A composite oxidation resistant refractory article comprising a porous niobium skeleton having a low melting alloy dispersed therethrough, said alloy comprising, by weight, 5% to 20% chromium, 0 to 20% silicon, 0 to 10% titanium, and the balance aluminum.

3. A composite oxidation resistant refractory article comprising a porous niobium skeleton having a low melting alloy dispersed therethrough, said alloy comprising, by weight, 5% to 20% chromium, 0 to 20% silicon, 3% to 5% titanium, and the balance aluminum.

4. A composite oxidation resistant refractory article comprising a porous niobium skeleton having a low melting alloy dispersed therethrough, said alloy comprising, by weight, 10% chromium, 3% silicon, 5% titanium, and the balance aluminum.

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