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[54] VANADIUM-BASE ALLOY

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[58] **Field of Search** ....75/134 V

[56] **References Cited**

OTHER PUBLICATIONS

W. Rostoker, " The Metallurgy of Vanadium," New York, Wiley, 1958, pp. 86 and 87 relied on.

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[57] ABSTRACT

An alloy contains 0.1–2.8 percent of at least one of the elements titanium, zirconium, and hafnium, traces to 2 percent silicon, traces of 4 percent germanium, balance vanadium, traces of usual metallic impurities which are due to the manufacturing process and, based on the vanadium content, 400–4,000 p.p.m. oxygen, 100–1,500 p.p.m. nitrogen, and 100–1,500 p.p.m. carbon, the total of oxygen, nitrogen, and carbon being not in excess of 5,000 p.p.m.

6 Claims, No Drawings

VANADIUM-BASE ALLOY

This invention relates to a vanadium-base alloy which is free of columbium and has low contents of titanium and/or zirconium and/or hafnium. The vanadium-base alloy according to the invention containing less than 2.8 percent titanium and/or zirconium and/or hafnium can be used in nuclear reactors as a structural material or for cladding fuel elements.

Vanadium-base alloys are known which consist substantially of 15–60 percent columbium, 3–25 percent titanium, balance vanadium (Canadian Pat. No. 716,521). Owing to their mechanical properties at elevated temperatures and their high resistance to corrosion in aqueous and gaseous fluids they are used as a material for propulsion systems of aircraft and spacecraft and for nuclear reactors. Binary vanadium-base alloys are known which contain 5 percent titanium or 2.8 percent titanium (Journal of the Less Common Metals, Vol. 12, 1967, pages 280–93). The vanadium-base alloy containing 5 percent titanium has shown good creep-rupture properties in tests carried out for as much as 1,000 hours.

It is an object of the invention to provide a vanadium-base alloy which has a good creep-rupture strength in prolonged tests and which is particularly suitable in nuclear reactors as a structural material or for cladding tubes and has a creep-rupture strength which is suitable for such use during a time of more than 10,000 hours.

This object is accomplished according to the invention by a substantially binary vanadium-base alloy, which is characterized by the following composition:

At least one of the elements titanium, zirconium or hafnium in an amount of 0.1 percent to less than 2.8 percent, preferably 1–2.5 percent, balance vanadium in conjunction with 400–4,000 p.p.m. oxygen, 100–1,500 p.p.m. nitrogen, and 100–1,500 p.p.m. carbon, the total of oxygen, nitrogen and carbon being not in excess of 5,000 p.p.m., and with small amounts of usual metallic impurities, such as nickel, iron, chromium and copper, which are due to the manufacturing process.

The term "usual metallic impurities" relates to such p.p.m., which are contained in the vanadium as a result of the manufacturing conditions. Each of these impurities is present in an amount not in excess of 1,000 p.p.m. e.g., up to 700 p.p.m. of each of the elements iron, chromium and nickel and up to 300 p.p.m. copper.

In the alloys according to the invention, the elements titanium, zirconium and hafnium may be present individually or jointly in the content range according to the invention. Contents of zirconium and/or hafnium in conjunction with titanium increase the resistance to oxidation. Where an additional improvement in ductility is desired it will also be desirable to replace the titanium content of the alloy according to the invention entirely or partly by zirconium and/or hafnium. Vanadium-base alloys which contain zirconium and/or hafnium have, e.g., the composition:

1 percent hafnium or zirconium
400–800 p.p.m. oxygen
200–600 p.p.m. carbon
200–600 p.p.m. nitrogen, balance vanadium with impurities consisting of about 300 p.p.m. of each of the elements iron, nickel, and chromium and about 100 p.p.m. copper.

The vanadium-base alloys in the composition range according to the invention contain as nonmetallic substances the elements carbon, nitrogen and oxygen in amounts totaling not more than 5,000 p.p.m. These elements amount preferably to 200–600 p.p.m. carbon, 200–600 p.p.m. nitrogen and 400–1,500 p.p.m. oxygen. The inherent embrittling action of these elements on the vanadium-base alloy is largely eliminated by the addition of titanium, zirconium and/or hafnium. The hard phases which are thus formed result also in a grain refinement and in an improved creep-rupture strength. In this connection, oxygen has a particularly important function, as is apparent from the following creep-rupture data:

Load kg./sq.mm.	Life in hours at 850° C. Vanadium + 2.5% titanium + 50 p.p.m. oxygen	Vandium + 2.5% titanium + 100 p.p.m. oxygen
12	–	70
10	9	83
6.5	100	–
3.5	1000	–

Each alloy contained 300–500 p.p.m. of each of the elements nitrogen and carbon as well as the following impurities which were due to the manufacturing process: 300 p.p.m. iron, 300 p.p.m. nickel, 300 p.p.m. chromium, 100 p.p.m. copper.

Silicon and/or germanium may be added to further improve the strength properties of the alloy according to the invention. This is apparent from the creep-rupture data in the following table:

Load kg./sq.mm.	Life in hours at 850° C. Vanadium + 2.5% titanium	Vanadium + 2.5% titanium + 1% silicon
9	–	1000
10	83	–
12	70	–
14	–	100
20	–	6

Each of the two alloys contained 300–500 p.p.m. nitrogen, 300–500 p.p.m. carbon and the following impurities which were due to the manufacturing process: 300 p.p.m. iron, 300 p.p.m. nickel, 300 p.p.m. chromium, 100 p.p.m. copper.

It is generally sufficient for a considerable improvement to add silicon in an amount of 0.1–2 percent, preferably 0.5–1.5 percent. Contents of 0.5–4 percent, preferably 1–3 percent germanium act in the same sense. Germanium may be used alone or in conjunction with silicon.

An alloy which has shown particularly desirable creep-rupture properties in a prolonged test at temperatures of 600°–800° C. has the following composition:

1.0–2.5 percent titanium
400–800 p.p.m. oxygen
200–600 p.p.m. carbon
200–600 p.p.m. nitrogen
balance vanadium and impurities consisting of about 300 p.p.m. of each of the elements iron, nickel, and chromium and about 100 p.p.m. copper.

Such alloy containing 1 percent titanium has a surprisingly high creep-rupture strength. Having a life of 1,000 hours under a load of 52 kg./sq.mm. at 650° C. and a life of 10,000 hours under a load of about 40 kg./sq.mm. at 650° C., it is superior to any previously known vanadium-base alloy which contains titanium or titanium and columbium.

This remarkably high creep-rupture strength is obtained without the presence of columbium, which would also increase the strength. The neutron economy of such alloys is much better than that of alloys which contain columbium.

The vanadium-base alloys according to the invention may be made by known metallurgical processes, e.g., in that the components of the alloy are fused together under a vacuum or in a rare gas atmosphere or by powder-metallurgical sintering processes. Suitable melting furnaces include, e.g., electron beam furnaces or arc furnaces. Known processes including extruding, forging, rolling and drawing may be used to manufacture shaped parts from the alloys according to the invention.

The vanadium-base alloys in the composition range according to the invention have advantages. The surprisingly high creep-rupture strength, the small neutron capture cross section, the low embrittlement which is caused by an irradiation with neutrons at temperatures of 600°–800° C., the high resistance to corrosion by liquid alkali metals and the high deformability of the alloys are decisive requirements for the use of such alloys as a material for structural elements and as a cladding material for fuel elements in nuclear reactors. The vanadium-base alloys in the composition range according to the invention can be used to special advantage as a material for structural elements which have a high creep-rupture strength at temperatures between 500° and 1,000° C., preferably between 600° and 800° C., in conjunction with a high resistance to corrosion by liquid alkali metals, particularly sodium, a small tendency to become embrittled by the irradiation with neutrons at temperatures between 600° and 800° C. and a small neutron absorption, or any individual one of these properties. Finally, the alloys in the composition range according to the invention can well be formed at elevated temperatures because they have a lower resistance to deformation than alloys which contain columbium.

Alloys in the composition range according to the present invention are used particularly as a material to make structural elements and as a cladding material for fuel elements in nuclear reactors, particularly in sodium-cooled fast breeders.

The high resistance of the alloy according to the invention to corrosion enables the use of this alloy in chemical engineering. Owing to its high strength at elevated temperatures in conjunction with its relatively low density, the alloy is interesting as a material for aircraft and spacecraft.

In the following table, the creep-rupture behavior of an alloy in the composition range according to the invention is compared to that of a vanadium-base alloy which contains titanium and columbium:

Life hours	Creep-rupture strength Vanadium + 2% titanium	in kg./sq. mm. Vanadium + 2% titanium +15% columbium
100	50	67
1000	40	52
10000	36	40

The test was carried out at a temperature of 650° C.

Both alloys contained 600–800 p.p.m. oxygen, 400–600 p.p.m. carbon, 300–500 p.p.m. nitrogen and in the vanadium the following impurities: About 300 p.p.m. of each of the elements iron, nickel, chromium, about 100 p.p.m. copper.

The strength data indicate that the vanadium-base alloy which is free of columbium has a lower strength at the beginning of the test and that the difference is progressively reduced as the required life is increased.

What is claimed is:

1. A vanadium-base alloy consisting of
0.1–2.8 percent of titanium,
traces to 2 percent silicon,
balance vanadium, traces of usual metallic impurities which are due to the process of producing the vanadium and, based on the vanadium content, 400–4,000 p.p.m. oxygen, 100–1,500 p.p.m. nitrogen, and 100–1,500 p.p.m. carbon, the total of oxygen, nitrogen, and carbon being not in excess of 5,000 p.p.m.

2. An alloy as set forth in claim 1, which contains 1–2.5 percent of titanium.

3. An alloy as set forth in claim 1, which contains, based on its vanadium content, 400–1,500 p.p.m. oxygen, 200–600 p.p.m. nitrogen, and 200–600 p.p.m. carbon.

4. An alloy as set forth in claim 1, in which said metallic impurities comprise at least one of the elements nickel, iron, chromium, and copper.

5. An alloy as set forth in claim 1, which contains at least 0.1 percent silicon.

6. An alloy as set forth in claim 1, which contains 0.5–1.5 percent silicon.

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