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FUEL ELEMENT FOR NEUTRONIC REACTORS

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This invention deals with bodies of niobium-base alloys and with fuel elements for neutronic reactors as they are described, for instance, in U.S. Patent 2,708,656, granted to Fermi et al. on May 17, 1955.

This application is a continuation-in-part of our copending application, Serial No. 538,816, filed on October 5, 1955, and now abandoned.

Iron-, nickel- or cobalt-base alloys have been investigated for the purpose described; however, these alloys were found to lose strength too rapidly at temperatures above 1800° F., temperatures prevailing, for instance, in the neutronic reactors mentioned above. Furthermore, the metals of the IVB, VB and VIB groups as defined in "Fundamental Chemistry" by Denning, which are transition metals, namely, titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, and tungsten have been tried for the above-mentioned purposes on account of their high melting points but they were found to require protection from oxidation. Molybdenum has the drawback that it readily forms molybdenum trioxide which melts and sublimes at 1463° F.; this molybdenum trioxide is a strong oxidizing agent and rapidly attacks other metals, for instance, many of the cladding metals used for protection against oxidation. Chromium has a good resistance to oxidation but is very brittle. Tungsten and tantalum are not well suitable for airplane reactors on account of their very high density.

The use of niobium metal has also been investigated because its density (8.57 g./cm.^{3}) is not too high, and it has a considerable strength at elevated temperature (however, only modest strength at room temperature), a low thermal-neutron-capture cross section (1.1 barns), a satisfactory ductility and thus good workability, and it also bonds well to cladding metals. However, niobium showed the disadvantages that the arc-melted metal could not be cold-worked easily and that the contents of contaminants such as oxygen and nitrogen had to be limited because they impair the workability. Niobium that had been arc-melted in a helium atmosphere, for instance, could be rolled at 1850° F. and at 2200° F., but it could not be rolled at 1000° F. or at room temperature.

It is an object of this invention to provide niobium alloys which have improved strength at elevated temperature, in particular between 1800° F. and 2200° F., as compared with the strength of elemental niobium in said temperature range.

It is another object of this invention to provide niobium alloys which are not only rollable at temperatures between 1800° F. and 2200° F. but also at room temperature.

It is furthermore an object of this invention to provide niobium alloys which have a high degree of hardness at elevated temperatures.

It is finally also an object of this invention to provide niobium alloys which have a low thermal-neutron-capture cross section.

These objects are accomplished by allowing at least one metal from the above-listed transition groups with the niobium. Binary alloys having a transition-metal content of from 5 to 15% by weight bring about the advantages of this invention; titanium was the preferred metal,

and a content of about 10% gave the very best results. (All percentages in this specification are given as percentages by weight.)

The alloys of this invention can be prepared by any method known to those skilled in the art. Arc-melting using a permanent or a consumable electrode has been found satisfactory. For instance, buttons of the alloy weighing between 50 and 75 g. were melted in an arc furnace on a water-cooled copper hearth, using a tungsten electrode. The power required varied from 500 to 1000 amperes D.C. An atmosphere of 10 p.s.i.a. of high-purity grade tank helium was supplied to the melting chamber after a number of evacuating and purging cycles. The buttons obtained were then remelted in a rectangular copper crucible of a capacity of 7.5 cm.^{3}.

In other instances a consumable electrode was used. For example, the starting electrode consisted of a 5/8-inch thick niobium rod to which 4 titanium rods of 0.143 diameter had been spot-welded. The assembled electrode was butt-welded to a zirconium adapter for the arc furnace. The ingots were cast in a right cylinder 1⅞ inch in diameter. A helium atmosphere was provided in the melting chamber after repeated evacuation and purging with helium. The arc was struck on a button of the same niobium alloy that had been placed in the bottom of the water-cooled copper crucible. In the case of titanium, for instance, at 1450 amperes the electrode was melted in 1 minute; about 450 grams of alloy were usually obtained. The titanium, or other metal of addition, was almost completely alloyed with the niobium. The hardness of the alloy in the case of 10% titanium was 192 DPHN (diamond pyramid hardness number). In order to improve the homogeneity of the alloy it was remelted.

Sintering of the metals in powdered form has also been found suitable for the preparation of the alloys of this invention.

The alloys were subjected to various types of tests in order to examine their suitability for the intended purposes. The oxidation resistance, for instance, was examined by exposing the binary niobium alloys and elemental niobium to air at 1800° F. for 2 hours and determining the increase in weight. Analyses of the alloys were carried out spectrographically. The results are compiled in Table I.

TABLE I

Alloy Addition, w/o	Total Area, in.^{2}	Weight Gain, g. per cm.^{2}
None	0.4044	1.192
1.61 Mo	0.4648	0.075
4.12 Mo	0.5420	0.053
1.83 Ta	0.3588	0.400
3.55 Ta	0.4018	0.466
8.9 Ta	0.4026	0.475
14.3 Ta	0.3994	0.519
5.0 Ti	0.3324	0.239
11.6 Ti	0.4336	0.113
16.5 Ti	0.4588	0.083
5.53 V	0.4232	0.097
10.3 V	0.4518	0.642
15.4 V	0.4744	0.846
2.1 Zr	0.3678	0.792
5.4 Zr	0.3856	0.963
10.4 Zr	0.4204	0.926
15.4 Zr	0.3916	0.688

This table shows that all of the alloying ingredients improve the resistance of the niobium to oxidation and that molybdenum has the most favorable effect. After molybdenum, titanium was the most beneficial component, in particular when it was added in quantities of about 11 and 16%, respectively.

The high-temperature strength was ascertained by short-time stress-rupture tests. These tests were carried

out in a helium atmosphere of slightly positive pressure at 2200° F. The specimens were held at this temperature for 15 minutes before they were subjected to stress. The stress was exerted by means of a pneumatic calibrated cylinder into which compressed air was introduced in steps of 1 p.s.i.; this was equivalent to a load on the specimen of about 1.5 lb. The elongation of the specimen was noted by a pointer arrangement. When sustained elongation was observed, further loading was discontinued and the specimen was allowed to elongate to rupture. The time for rupture varied from 0.1 to 0.3 hr.

The workability was determined by rolling 25-gram pieces, cut from rectangular arc-melts, in an unjacketed condition at 1850 and 2200° F. from a helium atmosphere furnace. A reduction of 10% in area was made per pass until a final reduction of 50% had been reached. A 15-minute reheat was used between passes, and the specimen was examined for cracks after each pass.

The cold-workability was tested by cold-forging 50-gram square-cut samples of arc-melted alloys after they had been machined on the top and the bottom. Cold-forging was continued until about 50% reduction in the cross-sectional area had been obtained; the specimens were then cold-rolled for another 50% reduction. In the cold-rolling procedure a reduction of 5% was effected per pass.

The hardness of the alloys was tested at room temperature and at 1600° F. (The type of mounting of the indenter prevented testing at temperatures above 1600° F.) A special hardness tester was employed which used a Vicker's type indenter under a 0.87-kg. load. Four or five runs were made for each specimen in the hot-hardness tests.

In the following some examples are given which illustrate the utility of the new alloys.

Example I

Niobium and binary niobium alloys having varying types and quantities of alloying components were tested as to workability and hardness, the tests used being those described above. The alloys had been made by arc-melting using a tungsten electrode, and the niobium used in all instances of this example was sheet niobium containing 0.02% of carbon. The results of these tests are compiled in Table II.

TABLE II

Added Element, Nominal w/o	Workability Rating[a]		Hardness, DPHN	
	Rolled at 1,850° F.	Rolled at 2,200° F.	Room Temperature	1,600° F.
None[b]			140	63
None[c]	E		164	75
5 Cr	NG	P		
10 Cr	NG	NG		
15 Cr	NG	NG		
2 Mo	F	F	184	89
5 Mo	P	P	152	134
10 Mo	P	P		
15 Mo	NG	NG		
2 Ta	E	F	163	84
5 Ta	F		190	153
10 Ta	P	F		
15 Ta	P	F		
5 Ti	E	E	155	102
10 Ti	E	E	236	156
12.5 Ti	E	E	199	124
15 Ti	E	E	251	143
20 Ti	E	E	260	126
5 V	P	P		
10 V	NG	NG		
15 V	P	P		
5 Zr	P	F	207	99
10 Zr	F	P		
15 Zr	F	P		

[a] E=no cracks; F=small cracks, essentially sound; P=large cracks; NG=broken.
[b] Arc-melted niobium, as cast.
[c] Arc-melted niobium, rolled at 1,850° F.

The only alloys which showed satisfactory workability at both temperatures plus improved hardness over that of niobium are the titanium-containing alloys. But all alloys tested yielded improved hardness values. Similar experiments carried out on a larger scale yielded the same favorable results.

Example II

Tests were made to roll the alloys of this invention at temperatures lower than 1850° F. A reduction of 10% was effected until the total reduction was 50%. Unjacketed arc-melted samples having a titanium content of 10% and taken from a helium-atmosphere furnace were tested at 750°, 1000°, 1250° and 1500° F. The best results were obtained at 1000° F., these specimens not containing any edge or surface cracks. This represents an improvement over the workability of metallic niobium which could not be rolled at such low temperatures without cracking.

Example III

This example demonstrates the improvement of cold-workability brought about by alloying the niobium with titanium. A niobium-titanium button containing 10% of titanium and produced by arc-melting was forged at 1000° F. until the reduction accomplished was about 75%; the thickness of the forged piece was 0.1 in. The piece was annealed for 2 hrs. at 2000° F. in a vacuum and then cold-rolled, at room temeprature, to a total reduction in area of 95%. The reduced sample showed no cracks. The hardness had increased with increasing reduction up to 50% reduction; hardness tests above 50% reduction could not be carried out because of the thinness of the material.

Example IV

Additions of 2% by weight of molybdenum, tantalum and tungsten, respectively, were made to the 10%-titanium alloy by arc-melting. The alloys thus obtained were rolled unjacketed at 1000° F. and 1250° F. All these alloys cracked on an initial reduction of 5% which shows that the ternary alloys do not have the advantageous characteristics of the binary titanium alloys.

Example V

Binary niobium alloys containing 2, 5, 10, and 15% by weight of zirconium were produced from high-purity sintered niobium by the arc-melting method and cast into rectangular shapes. The ingots were rolled in unjacketed condition from a helium-atmosphere furnace at 1250° F. accomplishing 5% reduction per pass. The specimens cracked extensively after a reduction ranging between 7 and 21%, the workability decreasing with increasing zirconium content. This example illustrates that zirconium does not bring about the same improvement which titanium accomplishes as to hot-workability.

Example VI

Short-time stress-rupture tests were conducted on niobium, binary niobium alloys containing varying amounts of titanium, on tantalum and on molybdenum. The niobium-titanium specimens were prepared from 32-cm.^{3} arc-melts which had been rolled unjacketed to strip at 2200° F. from a helium-atmosphere furnace, surface-ground and machined. The specimens were 10½ in. long and 0.025 in. thick with a gauge length of 2 in. Spectrographic analyses were made from the gauge length of each alloy specimen after testing. In addition to specimens of the hot-rolled alloys, other specimens were machined from a niobium alloy containing 9.7% of titanium which had been rolled at 1000° F., recrystallized and cold-reduced by 80%. The niobium test pieces were taken from a strip of commercially produced niobium which had been cold-rolled to approximately a 90% reduction in area. The molybdenum specimens were taken from a sheet which had been recrystallized at 2550° F., hot-rolled and finished cold. Tantalum samples were

ground from cold-rolled sheets. The results of these short-time stress-rupture tests are listed in Table III. Both series of values, those for rupture-stress and those for elongation, are averages taken of two parallel tests.

TABLE III

Alloy Nominal Composition, w/o	Spectrographic Analysis, w/o	Rupture Stress, p.s.i.	Elongation in 2 In., percent
Niobium		14,800	15.5
95 Nb–5 Ti [a]	5.0 Ti	16,000	11
90 Nb–10 Ti [a]	9.6 Ti	16,700	18
90 Nb–10 Ti [b]	9.7 Ti	15,700	32
85 Nb–15 Ti [a]	13.4 Ti	14,100	23
85 Nb–15 Ti [a]	14.0 Ti	10,200	33
Molybdenum		18,000	3
Tantalum		9,400	46

[a] Arc-melted and hot-rolled alloy.
[b] Arc-melted and cold-rolled alloy.

These results indicate that additions of titanium increase the strength of niobium at 2200° F., the maximum improvement occurring at a titanium content of 10%.

Cores for fuel elements for neutronic reactors were made by embrittling scrap sheet niobium in hydrogen for 1 hour at 850° F., powdering the niobium, and then dehydriding it by heating to 2000° F. Fissionable material and titanium were then added to the niobium powder; in one instance, for example, 67.5 parts by weight of niobium powder were mixed with 7.5 parts by weight of titanium and 25 parts by weight of uranium dioxide powder, and the mixture was then pressed at 30 t.s.i. The cores thus obtained were clad with a corrosion-resistant alloy. As cladding metal, for instance, the chromium-aluminum-iron alloys proved satisfactory that contain from 15 to 30% by weight of chromium, from 5 to 6.5% of aluminum, from 1 to 10% of at least one metal selected from the group consisting of niobium and tantalum, the balance being iron. The fuel element cores of this invention can also be clad by a binary zirconium-tin alloy in which the tin content ranges between 1 and 15% by weight; this alloy is claimed in application Serial No. 265,018, filed by Henry A. Saller et al. on January 4, 1952, and granted as U.S. Patent No. 2,813,073 on November 12, 1957.

Example VII

A series of powder compacts made as described in Example VI and containing varying amounts of niobium, titanium and uranium dioxide were sintered at 2600°, 2800° and 3100° F. and then reduced by cold-hammering until the specimens broke or cracked extensively. The results are given in Table IV.

TABLE IV

Composition, w/o	Sintering Temp., °F.	Average Cold Reduction at Breakage or Cracking, percent
100 Nb	2,600	38
	2,800	38
	3,100	48
90 Nb–10 Ti	2,600	65
	2,800	73
	3,100	59
85.5 Nb–9.5 Ti–5 UO_2	2,600	73
	2,800	56
	3,100	53
81 Nb–9 Ti–10 UO_2	2,600	15
	2,800	35
	3,100	37
76.5 Nb–8.5 Ti–15 UO_2	2,600	44
	2,800	27
	3,100	38
72 Nb–8 Ti–20 UO_2	2,600	18
	2,800	24
	3,100	39
67.5 Nb–7.5 Ti–25 UO_2	2,600	15
	2,800	35
	3,100	24

These experiments show that niobium metal has a good ductility but that it is considerably improved by alloying with titanium. The higher contents of uranium dioxide impair the ductility.

Example VIII

A series of clad packs containing cores of niobium, niobium—10% titanium, niobium—9.5% titanium—5% UO_2, and niobium—7.5% titanium—25% UO_2 were hot-pressed and rolled at 2200° F. A ternary iron alloy containing 25% of chromium and 5% of aluminum was used as the cladding material. These packs were pressed for 15 minutes at 2000 p.s.i. in a graphite die at 2200° F. and then rolled at the same temperature at a reduction of 25% per pass to a total reduction of 90%. Metallographic examination revealed that all cores, except that of pure niobium, bonded well; however, the core containing 25% of uranium dioxide had broken extensively on rolling.

Example IX

50-g. square-cut samples of arc-melted binary niobium alloys were machined on the top and the bottom and then cold-forged to about 50% reduction in cross-sectional area or until cracked; the thickness then was about 0.15 in. Thereafter the samples were cold-rolled to half the thickness without any intermediate annealing step; 5% reduction was carried out per pass. The compositions of the alloys and the workability are given in Table V.

TABLE V

Alloying Component, w/o	Cold-Forging		Cold-Rolling	
	Reduction, percent	Results	Reduction, percent	Results
1.61 Mo	57	Very good	50	Very good.
4.12 Mo	51	do	51	Do.
8.2 Mo	50	Several small edge cracks.		Broken.
13.5 Mo	48	Edge cracks		
1.83 Ta	54	Very good	53	Very good.
3.55 Ta	65	do	54	Do.
8.9 Ta	58	do	53	Do.
14.3 Ta	56	do	50	Do.
5.0 Ti	50	do	50	Do.
11.6 Ti	44	do	44	Do.
16.5 Ti	48	do	48	Do.
5.53 V	47	do	47	Do.
10.3 V	45	do	45	Small edge cracks.
15.4 V	46	Slight edge cracks.	46	Do.
2.1 Zr	56	Very good	52	Very good.
5.4 Zr	55	do	52	Small edge cracks.
10.4 Zr	58	Slight edge cracks.	51	Do.
13.4 Zr	59	Large edge cracks.	49	Do.

It is obvious from this table that all alloys except those having a higher molybdenum and a higher zirconium content have good cold-workability.

It will be understood that this invention is not to be limited to the details given herein but that it may be modified within the scope of the appended claims.

What is claimed is:

1. A fuel element for neutronic reactors having a core consisting of uranium dioxide embedded in a binary niobium-base alloy containing from 5 to 10% by weight of titanium and a jacket of a corrosion-resistant alloy around said core.

2. The fuel element of claim 1 wherein the titanium content is about 10%.

3. The fuel element of claim 1 wherein said corrosion-resistant alloy is an iron-base alloy which contains from 15 to 30% by weight of chromium, from 5 to 6.5% of aluminum, from 1 to 10% of at least one metal selected from the group consisting of niobium and tantalum, the balance being iron.

4. The fuel element of claim 2 wherein uranium dioxide is present in a quantity of about 5% and the jacket is securely bonded to said core.

5. The fuel element of claim 4 wherein said corrosion-resistant alloy is an iron-base alloy which contains from 15 to 30% by weight of chromium, from 5 to 6.5% of aluminum, from 1 to 10% of at least one metal selected from the group consisting of niobium and tantalum, the balance being iron.

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