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2,736,651

ZIRCONIUM TERNARY ALLOYS

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No Drawing. Application August 19, 1954,
Serial No. 451,076

2 Claims. (Cl. 75—177)

The present invention is concerned with zirconium base alloys and particularly with zirconium-tin base ternary alloys.

The development of nuclear reactors for power applications and of cyclotrons, linear accelerators and similar apparatus subject to radioactivity and high temperatures has caused a demand for novel alloys having good high-temperature strength and low neutron-absorption characteristics for structural members in such apparatus. The strength characteristics of these new alloys should be approximately as good as the characteristics of the stainless steels normally used in high-temperature devices, but the alloys should have a much lower neutron capture cross section than the stainless steels. Furthermore, the alloys must have sufficient workability to enable them to be fabricated into simple shapes.

While such elements as aluminum, lead, molybdenum, niobium, tantalum, tin, titanium and vanadium can all be used to strengthen zirconium effectively in binary alloys, it has been found in general that reasonable strength can be achieved only by sacrificing ductility or by increasing the thermal-neutron capture cross section of the alloy to an undesirable extent. This results from the fact that no element has been found as yet which has the combination of a high solubility in alpha zirconium, a low thermal-neutron capture cross section, and a satisfactorily high boiling point.

It is an object of the present invention to provide novel alloys having strength characteristics at high temperatures approximately equivalent to that of stainless steel, but having neutron capture cross sections less than one-third that of stainless steel.

In accordance with the present invention, it has been found that novel zirconium base ternary alloys containing tin and a third metal from the group consisting of aluminum and the members of the V-B group of the periodic table, namely, vanadium, niobium and tantalum, have desirable strength characteristics at high temperatures and have low thermal-neutron capture cross sections. The tin component of these ternary alloys may range from about 1 to 6 w/o (weight percent) and the third component of the zirconium-tin alloys from 0.1 to 4 w/o.

Zirconium is a transition element, characterized by an incomplete inner shell of *d* electrons and an allotropic transformation at 865° C., transforming from a hexagonal crystal structure into a high-temperature body-centered cubic structure. The primary effect of the small addition of a group V-B element is to depress this transformation temperature, while tin and aluminum have a tendency to increase this temperature. Thus tin and aluminum may be regarded as stabilizers of the alpha phase of zirconium alloys, and the group V-B elements

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as beta phase stabilizers. It has been found that in ternary zirconium alloys the hardness at elevated temperatures is controlled largely by the beta stabilizers present, and the softening temperature is a characteristic of the amount of alpha stabilizers present. Within limits the beta stabilizers merely change the hardness at the softening temperature. Therefore superior high-temperature alloys are obtained, as in the present alloys which contain a V-B group type element, by including a small amount of a beta stabilizer and a larger amount of an alpha stabilizer. The resultant alloy has a high softening temperature, and is easily fabricated at high temperatures.

The alloys may be produced by conventional methods. For the experiments described below the alloys were prepared by drilling holes in a piece of metallic zirconium, putting suitable quantities of the two minor metal components into these holes and then filling the holes with zirconium chips. Zirconium pieces formed in this manner were then heated in a graphite crucible by high-frequency induction at an absolute pressure of less than 10 microns of mercury. A charge of about 200 grams was melted in each case; the crucible was first charged with about half this quantity and only after this portion had melted was there added the remainder of the charge. The melted alloy was then allowed to cool slowly. The ingots obtained thereby weighed between 160 and 180 grams, part of the material having been taken up by the graphite of the crucible.

The alloys were also produced in arc-melting furnaces and satisfactory results were obtained by this method. During the melting in the graphite crucible, a small amount of carbon, up to about 0.5 w/o, was picked up by the alloys. A comparison of the arc-melted alloys and the induction melted alloys shows a very definite trend in favor of arc-melting for improving the strength of the alloys at high temperatures. A comparison of the tensile strengths of zirconium-tin-aluminum alloys, one prepared by arc-melting and the other by induction-melting, is shown in Table I.

TABLE I

500° C. tensile properties of zirconium alloys

Melting Method	Alloy Analysis, w/o (Balance Zr)	0.2% Offset Yield Strength, p. s. i.	Ultimate Tensile Strength, p. s. i.	Elongation in 1 in., percent	Reduction in Area, percent
Arc-----	3.4 Sn+0.5 Al---	44,200	55,100	11	8
Induction-----	3.4 Sn+0.6 Al---	32,300	34,400	4	6

The various novel alloys produced were tested at 500° C. for hardness, tensile strength and elongation, the characteristics primarily of interest for structural materials. For hardness tests the ingots of the alloys were first upset-forged and then hot-rolled at 1000° C. to yield 1/8-inch thick slabs. Then about 0.01 inch of the slabs was shaved off from the surface on each side in order to remove any gaseous contaminants. The "scalped" slabs were then cold-rolled in reductions of approximately 0.002 inch per pass until a total reduction of from 20 to 30% had been obtained. The cold-rolled alloys were then annealed for one hour at 700° C. in a straightening press. The sheaths resulting thereby were again "scalped" 0.018 inch on one side and cut into testing specimens.

The hardness was determined at three stages of the

alloys, namely, as cast, cold-rolled, and annealed, and the results are tabulated in the following table.

TABLE II
Hardness data for zirconium alloys

Alloy Analysis, w/o	Rockwell A Hardness		
	As Cast	Cold-Rolled	Annealed
2.8 Sn + 0.46 Al	52	58	56
3.7 Sn + 0.4 V	51	60	57
5.4 Sn + 0.6 V	55	62	58
4.3 Sn + 1.0 V	53	60	57
4.1 Sn + 0.3 Nb	52	59	54
3.8 Sn + 1.0 Nb	52	59	55
4.6 Sn + 0.66 Ta	45	58	55
1.2 Al	50	61	58
2.0 Al	37	59	57

For the tensile strength tests specimens 5 inches long, $\frac{5}{8}$ inch wide and 0.04 to 0.08 inch thick were prepared. The reduced section was 1.5 inches long and $\frac{1}{16}$ inch wide. The specimens were tested at 500° C. in an argon atmosphere. The speed of travel of the head of the testing machine was 0.02 inch per minute and an extensometer with a 1-inch gauge length and an accuracy of plus or minus 0.0001 inch per inch was used to measure extensions. The extensometer was of the clip-on type with slide bars extending out of the heated area around the specimen.

The results of these tensile tests are shown in Table III. The tests were run in duplicate on each alloy and the results shown in Table III represent the average values obtained from these tests. The values listed under "uniform elongation" represent the total elastic and plastic deformation at maximum load. The tensile strengths of the zirconium-aluminum binary alloys are shown for purposes of comparison.

TABLE III

Tensile properties of zirconium alloys at 500° C.

Zirconium Alloys, w/o (as analyzed)	0.2% Offset Yield Strength, 1,000 p. s. i.	Ultimate Strength, 1,000 p. s. i.	Total Elonga- tion, Percent in 1 inch	Reduction of Area, Percent
0.38 Al	18	30	31	34
0.87 Al	25	38	30	37
2.8 Sn + 0.46 Al	29.4	42	22	32
4.1 Sn + 0.3 Nb	24.2	35.7	32	22
3.8 Sn + 1.0 Nb	25.3	37.0	40	29
3.7 Sn + 0.4 V	25.1	38.2	37	44
5.4 Sn + 0.6 V	38.7	54.7	16	52
4.3 Sn + 1.0 V	30.2	41.1	25	36
2.2 Sn + 1.1 V	21.4	33.8	20	23
2.7 Sn + 1.9 V	21.0	36.2	21	33
4.6 Sn + 0.66 Ta	25.7	40.0	28	33

The creep strength of alloys intended for high-temperature use is very important since it is a measure of the resistance to deformation under a steady load at an elevated temperature. The test specimen is placed under a load and maintained at a particular temperature and the deformation is measured as a function of time. As a general rule, the strain takes place in three successive stages: first, an initial rapid rate stage lasting from a few hours to a few days; second, a secondary reduced rate stage, nearly linear with time, lasting for a comparatively extended period; and third, a final rapid rate stage terminating in rupture. Both arc-melted and induction-melted zirconium-tin-aluminum alloys were tested for creep strength and found to have very desirable characteristics, as is shown by the results tabulated in the following table. The approximate minimum creep rate is a measure of the rate of extension of the sample in the second or steady stage.

TABLE IV
Creep properties of zirconium alloys at 500° C.

Alloy Analysis, w/o (Balance Zr)	Stress at 500° C., p. s. i.	Approximate Minimum Creep Rate, Percent/hr.	Total Time, hr.	Total Deformation, Percent
3.4 Sn + 0.6 Al ¹	25,500	0.011	929	² 17.6
3.4 Sn + 0.5 Al ³	15,000	0.0012	1,632	2.7
	10,000	0.00025	1,400	0.58

¹ Induction-melted alloy.

² Indicates failure in grip section.

³ Arc-melted alloy.

The improved characteristics of the alloys of this invention for high-temperature reactor structural materials may best be illustrated by comparing the yield strengths and thermal-neutron capture cross sections of these materials with those of stainless steel and zirconium and zirconium-tin binary alloys. These ratios are shown in Table V.

TABLE V

Properties of zirconium alloys compared with properties of stainless steel at 500° C.

Alloy Analysis, w/o (Balance Zr)	Thermal-Neutron Capture Cross Section, barns/atom	Cross Section Ratio	Yield Strength Ratio
Stainless Steel, Type 347	2.86	1	1
Induction-Melted Zirconium	0.20	0.070	0.3
1.05 Sn	0.20	0.070	0.46
1.35 Sn	0.20	0.070	0.51
2.8 Sn + 0.46 Al	0.21	0.073	0.95
4.1 Sn + 0.3 Nb	0.22	0.077	0.78
3.8 Sn + 1.0 Nb	0.23	0.080	0.82
3.7 Sn + 0.4 V	0.24	0.084	0.81
5.4 Sn + 0.6 V	0.26	0.091	1.25
4.3 Sn + 1.0 V	0.29	0.101	0.97
2.6 Sn + 0.6 V	0.23	0.080	0.65
2.2 Sn + 1.1 V	0.27	0.094	0.69
2.7 Sn + 1.9 V	0.33	0.115	0.70
4.6 Sn + 0.66 Ta	0.28	0.098	0.83

It will be noted that the zirconium-tin-aluminum and two of the zirconium-tin-vanadium alloys have particularly good yield strengths. It was also found that the zirconium-3.8% tin-1.0% niobium alloy has very good corrosion resistance when exposed to water at a temperature of 360° C. for long periods. The three zirconium-tin-vanadium alloys having tin contents greater than 3.0 w/o also are corrosion-resistant to the attack of water at elevated temperatures.

While the characteristics of exceptional strength at high temperatures, creep resistance and low cross section make these alloys particularly valuable for use in structural components of nuclear reactors of the high-temperature type, the high temperature strength and creep resistance also make these alloys valuable for structural components in other high-temperature applications such as aircraft engines, jet engines, chemical process equipment, etc.

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 ternary zirconium base alloy containing 1 to 6 weight percent tin and 0.1 to 4.0 weight percent aluminum.

2. A creep-resistant zirconium alloy characterized by tensile strength equal approximately to stainless steel at elevated temperatures comprising 2.8 weight percent tin, 0.46 weight percent aluminum and the balance zirconium.

References Cited in the file of this patent

Muehlen Kamp et al.: U. S. A. E. C. Document, BM1-845 (June 30, 1953), 15 pages.

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