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ZIRCONIUM ALLOY TREATMENT PROCESS

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This invention relates to a novel process of making nuclear reactor components and more particularly to a process of increasing the corrosion resistance of nuclear reactor components that are made from zirconium base alloys that contain from 0.5% to 5% by weight of niobium and which may optionally contain up to 3% by weight of tin and which may also optionally contain in addition to tin up to 2% by weight of one of the metals: iron, nickel, chromium, tantalum, palladium, molybdenum, and tungsten.

Binary zirconium base alloys containing from 0.5% to 5% by weight of niobium have been used as components of nuclear reactors and more particularly as cladding for fuel elements that are subject to corrosion by pressurized water or steam. Such alloys are generally soft annealed at temperatures above 640° C., e.g. at 900° C., after a hot forming operation, but the metal structure thus obtained displays an unsatisfactory resistance to corrosion by hot pressurized water or steam. The corrosion resistance of these alloys is somewhat improved if the annealing operation at 900° C. is followed by quenching and then the alloys are further annealed at a temperature of 500° to 600° C. However, these additional steps still fail to give these alloys the desired degree of resistance to corrosion.

This invention has as an object the preparation of nuclear reactor components that are resistant to corrosion by steam or hot water and that are made from zirconium base alloys containing niobium. A further object of this invention is to provide a simple technique for increasing the corrosion resistance of reactor components made from zirconium base alloys containing niobium. Other objects will be apparent from the following description of the invention.

These objects are accomplished by the present invention which relates to the annealing at a temperature between 550° C. and 600° C. of articles made by cold shaping zirconium base alloys containing niobium immediately after said articles have been cold shaped. The zirconium base alloys to which the present invention pertains include binary zirconium-niobium alloys containing from 0.5 to 5% by weight of niobium, ternary zirconium-niobium-tin alloys containing from 0.5 to 5% by weight of niobium and up to 3% by weight of tin, and quaternary zirconium base alloys containing from 0.5 to 5% by weight of niobium, up to 3% by weight of tin, and up to 2% by weight of a fourth metal selected from the group consisting of iron, nickel, chromium, tantalum, palladium, molybdenum, and tungsten.

In order to improve the corrosion resistance of reactor components to be made from the zirconium base alloys hereinabove indicated, they are first cold shaped and subsequently subjected to a heat treatment between

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550° C. and 600° C. The term "cold shaping" is used to denote a shaping of the component within a temperature range in which no recrystallization of the structure takes place. Such cold shaping may therefore be performed at temperatures up to about 550° C. For practical reasons, the shaping is usually carried out at ambient temperatures. Prior to the cold shaping the component may have been soft annealed at temperatures between 640° C. and 1000° C. As an alternative procedure, the component may have been hot shaped at temperatures between 640° C. and 1000° C., and then either quenched or slowly cooled in air before being subjected to the cold shaping step of the present invention.

The duration of the annealing treatment applied in accordance with the present invention is determined by the temperature of annealing and also by the extent of reduction of the component. An article formed from a zirconium base alloy containing 1% by weight of niobium and reduced by 60% by cold shaping shows a considerable improvement in its corrosion resistance after a heat treatment at 575° C. for 60 minutes. If the annealing temperature is increased, the duration of the annealing treatment may be reduced. The duration of the annealing operation is not limited. However, the annealing operation is usually terminated when the desired improvement of the article's corrosion resistance has been achieved.

After annealing in accordance with the invention, the component is cooled or quenched as desired.

The heat treatments of the components at 550°-600° C. in accordance with the present invention are in the nature of final annealing treatments. No further annealing can be carried out which will nullify the improvement in corrosion resistance that has been attained. Therefore, while no harm will result from a short annealing treatment below 500° C., no annealing at temperatures in excess of 600° C. can be tolerated.

The heat treatments of the present invention are in all cases applied subsequent to cold shaping operations. However, several cold shaping operations may precede the heat treatment. Between these prior cold shaping operations the articles may be annealed at temperatures between 640° C. and 1000° C. in accordance with prior art practice. After a heat treatment in accordance with the present invention, a further cold shaping operation may be performed. However, such a shaping operation should be a minor one, involving a reduction of less than 20%. The heat treatments made in accordance with the present invention may also be applied as intermediate treatments between several cold shapings.

The process of the present invention imparts a pronounced improvement in the corrosion resistance of the zirconium base alloys thus treated as may be seen from the following examples.

EXAMPLE 1

Corrosion tests were carried out on sheets 1.8 mm. thick made from binary zirconium-niobium alloys containing 1% and 3% by weight of niobium. In one group of these tests the sheets were exposed to steam at 400° C. at a pressure of 200 atmospheres (2,845 pounds per square inch) for a period of 1500 hours. In another group of these tests the sheets were submerged in pres-

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surized water at 350° C. at saturation pressure for 1500 hours. The results of these tests are indicated below in Table 1. The data in line A of this table pertains to sheets that had been annealed at 900° C. for 2 hours and then quenched in water in accordance with a known prior art technique. The data in line B of this table pertains to sheets that had been annealed at 900° C. for 2 hours, quenched in water, reannealed at 575° C. for 48 hours and then cooled in air in accordance with known prior art practice. The data in line C of this table pertains to sheets that had been cold shaped to a 60% reduction and then annealed for 48 hours at 575° C. followed by air cooling in accordance with the present invention. Comparison of the data in line C with the data given on lines A and B shows the clear superiority of the present invention over prior art practices.

Table 1

[Increase in weight (mg. per dm.²)]

Line	Steam at 400° C.		Water at 350° C.	
	Zr-1% Nb	Zr-3% Nb	Zr-1% Nb	Zr-3% Nb
A-----	120	200	49	72
B-----	88	78	40	35
C-----	61	64	31	26

EXAMPLE 2

Test samples of a ternary zirconium base alloy containing 0.5% by weight of niobium and 1% by weight of tin were exposed to steam at 400° C. at a pressure of 200 atmospheres for a period of 1900 hours. One sample which was merely annealed for 24 hours at 700° C. showed an increase in weight of 123 mg. per dm.² after testing. The other sample was not only annealed for 24 hours at 700° C., but also cold shaped to 50% reduction at ambient temperature and then heat treated for 24 hours at 590° C. in accordance with the present invention. This latter sample showed only an increase in weight of 107 mg. per dm.² after testing.

EXAMPLE 3

Test samples of a ternary zirconium base alloy containing 2% by weight of niobium and 1% by weight of tin were exposed to steam at 400° C. at a pressure of 200 atmospheres for a period of 1900 hours. One sample that was merely annealed for 24 hours at 700° C. showed an increase in weight of 195 mg. per dm.² after testing. The other sample was not only annealed for 24 hours at 700° C., but also cold shaped to 50% reduction at ambient temperature and then heat treated for 24 hours at 590° C. in accordance with the present invention. This latter sample showed only an increase in weight of 120 mg. per dm.² after testing.

EXAMPLE 4

The following table gives the results of 500 hours of exposure to steam at 400° C. and at 480° C. of three quaternary zirconium base alloys containing niobium, tin and a fourth metal. The results in column A pertain to samples that have been heat treated for 1 hour at 650° C. and then cooled in air. The results in column B pertain to samples that have been reduced 50% by cold shaping followed by subsequent heat treatment for 240 hours at 575° C. in accordance with the present invention and then cooled in air. Comparison of the data in columns A and B shows the superiority of the present invention.

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Table 2

Composition of Zirconium Base Alloy	Steam Temperature, ° C.	Increase in Weight (mg. per dm. ²)	
		A	B
Zr-2% Nb-0.5% Sn-0.3% Cr-----	400	74	32
Zr-2% Nb-0.5% Sn-0.3% Cr-----	480	270	220
Zr-2% Nb-0.5% Sn-0.3% Mo-----	400	116	34
Zr-2% Nb-0.5% Sn-0.3% Mo-----	480	305	245
Zr-5% Nb-1% Sn-0.2% Pd-----	400	135	62

EXAMPLE 5

The quaternary zirconium base alloy containing 5% by weight of niobium, 1% by weight of tin, and 0.2% by weight of palladium was also submerged in pressurized water at 350° C. for 500 hours. The sample thereof that had been merely heat treated for 1 hour at 650° C. and then air cooled gained 77 mg. per dm.², but the sample thereof that had been reduced 50% by cold shaping followed by subsequent heat treatment at 575° C. for 240 hours in accordance with the present invention and then cooled in air gained only 47 mg. per dm.². This example further illustrates the advantage of the present invention.

Resort may be had to such modifications and variations as fall within the teachings of the above specification and the scope of the appended claims.

We claim:

1. A process of preparing zirconium base alloys of improved corrosion resistance for use in a nuclear reactor comprising making 50 to 60 percent reductions by cold shaping the zirconium base alloys selected from the group consisting of binary zirconium-niobium alloys containing from 0.5 to 5% by weight of niobium, ternary zirconium-niobium-tin alloys containing from 0.5 to 5% by weight of niobium and up to 3% by weight of tin, and quaternary zirconium base alloys containing from 0.5 to 5% by weight of niobium, up to 3% by weight of tin, and up to 2% by weight of a fourth metal selected from the group consisting of iron, nickel, chromium, tantalum, palladium, molybdenum, and tungsten, at a temperature not above 550° followed by an annealing of said cold shaped alloy at a temperature between 550° C. and 600° C. for a period of from 1 to 240 hours and subsequently air cooling whereby improved steam and hot water corrosion resistance is effected.

2. A process as recited in claim 1 in which the cold shaping is performed at ambient temperatures.

3. A process according to claim 1 in which the zirconium base alloys are hot shaped at 640° C. to 1000° C. and air cooled prior to cold shaping.

4. A process according to claim 1 in which the zirconium base alloys are soft annealed at 640° C. to 1000° C. and air cooled prior to cold shaping.

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