

[54] **METHOD OF MAKING TUBES AND
SIMILAR PRODUCTS OF A ZIRCONIUM
ALLOY**

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[58] **Field of Search**..... 148/11.5 F; 75/177

[56] **References Cited**

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[57] **ABSTRACT**

The creep strength of a tube formed from a "Zircaloy" material is improved by prefacing the final cold working step of the manufacturing procedure by heating the material to the β -range and then cooling to room temperature.

4 Claims, No Drawings

METHOD OF MAKING TUBES AND SIMILAR PRODUCTS OF A ZIRCONIUM ALLOY

The present invention relates to a method of making tubes, and other products, of zirconium alloys containing (in percent by weight) 1.2 - 1.7 Sn, 0.07 - 0.24 Fe, 0.05 - 0.15 Cr, 0 - 0.08 Ni, 0.09 - 0.16 O, balance zirconium and customary impurities, the same being known as the "Zircaloys" or specifically "Zircaloy 2" and "Zircaloy 4."

In the conventional production of "Zircaloy" tubes, for example, canning or cladding tubes used in the nuclear reactors, after melting and casting of the material there is a step of plastic working of the ingots up to final tube dimension. The working is usually started by forging in the α -range followed by so-called β -quenching which means heating to a temperature within the β -range and quenching in water to room temperature. Then extrusion is effected in the α -range, after which cold working is done in the form of a series of pilger rollings, drawings or similar operations, usually accompanied by intermediate annealings in the α -range.

By the expression " α -range" is meant the lower temperature interval wherein the close-packed hexagonal crystal lattice is stable, while the " β -range" means the higher temperature interval wherein the body-centered cubic crystal lattice is stable. In pure zirconium the boundary between the α - and β -ranges is at 862° C., while in all alloys there is a two-phase $\alpha + \beta$ range at around this temperature.

While most other zirconium alloys are processed in the same way as "Zircaloy," there is one exception: i.e., the zirconium-niobium alloys containing 1-5 percent Nb and up to 3 percent Sn. These alloys are specifically designed for high strength. The basic strengthening mechanism is a finely dispersed precipitation obtained through a quenchage treatment - the alloys being characterized as age-hardenable. In practice, the production of these alloys includes as the last steps a heat treatment in the β - or $\alpha + \beta$ -range followed by quenching in water to a martensitic structure, possible cold work for example by rolling or drawing, and aging or tempering in the α -range at around 500° C. A major concern for the zirconium-niobium alloys is their corrosion resistance in the nuclear reactor environment. This can be improved by proper selection of temperature and time in the quench-age treatment, as is known for example from a number of patent publications, in which the procedure for reaching optimum strength and corrosion properties is clarified.

The active constituent in the zirconium-niobium alloys is a secondary phase called " β -niobium." It consists essentially of niobium, thus requiring a high degree of segregation of niobium between the α -zirconium and β -niobium phases. The strong segregation provides for finely dispersed precipitation and resistance to coarsening, which is a basic prerequisite for an age-hardenable alloy. In contrast to this, most other zirconium alloys, and specifically "Zircaloy," have a secondary phase consisting essentially of zirconium and requiring a moderate segregation of the alloying elements tin, iron, chromium. In addition, the solubility in the α -phase of the "Zircaloy" alloying elements is great compared to that of niobium. This makes the precipitation hardening in "Zircaloy" weak, and the alloy has never been regarded as age-hardenable. There is no known process where "Zircaloy" is quench-aged in the

final production steps. The β -quenching described earlier is purely applied for corrosion reasons; moreover, it is done so early in the process that a possible strengthening effect is completely dissipated by the subsequent α -annealings. Instead, the conventional way of controlling the mechanical properties of "Zircaloy" tubing involves choosing the degree of cold work in the final rolling step and the temperature of the final annealing to give optimum conditions. This gives a work-hardened and a more or less recovered and recrystallized structure.

During operation of the reactor the canning tubes are required to possess both strength and ductility. In recent years, attention has been focused on the creep strength in the transverse direction of the tube at 300° - 400° C. The creep strength can be improved by adjusting the degree of cold work and the final annealing temperature, but with a sacrifice in production economy.

According to the present invention it has now been found possible to reach an essentially increased creep strength in "Zircaloy" tubes by means of a relatively simple modification of the manufacturing procedure. This modification means essentially that a heat-treatment similar to the quench-age treatment of zirconium-niobium is introduced also for "Zircaloy." Quenching may replace the last intermediate or soft annealing step, or it can be done immediately before or after it. The material is thus heated up to the β -range, usually 860° - 1,250° C., and preferably to a temperature between 1,000° - 1,150° C., after which cooling to room temperature is done. The cooling may be done by means of quenching in water, i.e., proper " β -quenching," or by air cooling. Also cooling at speeds lying between the corresponding speeds of the mentioned cooling methods may be used.

It is believed that the essentially improved creep strength is connected with the fact that the content of alloying elements in solution is increased by means of the mentioned heat-treating step according to the invention, which in its turn means an increased temperature for the maximum dynamic aging effect according to the following text.

In the earlier-mentioned "Zircaloy" β -quenching, which is generally done after forging, the cooling speed when quenching in water is not higher, because of the usually relatively large billet dimension, than that secondary phase particles are precipitated during the cooling. These particles which contain an essential part of occurring alloying elements grow during the following heating operations, at the same time as more secondary phase particles are precipitated. The content of alloying elements in solution thus becomes lower and lower during the conventional (heretofore used) manufacturing procedure.

By means of the heat-treating step according to the invention there is allotted a dissolution of secondary phase particles and the alloying elements which are bound in these particles is, therefore in solution to a larger extent than normally. Studies of so-called dynamic strain aging at plastic deformation of the "Zircaloy" alloy has shown that maximum dynamic aging effect, at strain rates corresponding to creep, is obtained at about 300° - 350° C. for material which has been manufactured in conventional ways. By the term "dynamic" is here meant that the aging process occurs simultaneously with the creep testing as opposed

to "static" aging in a special aging heat-treatment before testing described in the case of zirconium-niobium. By means of the method according to the invention it is possible to increase the temperature of the maximum ageing effect up to 400° C. by increasing the content of alloying elements in solution. Because this aging effect probably contributes to the high creep strength, it is realized that an increase of the temperature of the maximum aging effect means an increase of the creep strength. It is essential that the field of action of the maximum aging effect could be increased by means of the invention up to a critical temperature level of the cladding material, at which often certain requirements regarding the strength have been specified.

The method according to the invention has not caused any depreciation of the corrosion properties, which depreciation might have been expected in view of the earlier-mentioned influence of the secondary phase particles. The normal way of procedure is thus considered to give nearly optimum size and distribution of the particles in regard to maximum corrosion resistance of the alloy.

After the last cold working step a so-called final annealing of the material is normally done. The final annealing is done within the temperature range 400° - 700°C., at which in "Zircaloy" an annealing at temperatures between 400° to about 490° C. gives a recovered structure, annealing between about 490° to about 530° C. gives a partially recrystallized structure, and annealing at higher temperatures gives a completely recrystallized structure. In the method according to the invention it has been found advantageous to locate the annealing in the range of partial recrystallization 500° - 530° C. The idea is that this temperature is low enough to allow a considerable portion of the alloying elements to remain in solution.

The degree of reduction in the last cold working step influences the creep strength in the same way as without β -quenching. This means that the effect according to the invention is additive to the conventional effect of cold work, these being an incentive for high degree of cold work from production economy point of view. It has thus been found advantageous to reduce the cross-sectional area of the material at least 50 percent in the last cold working step. The properties at tensile and burst testing of tubing made according to the invention are essentially the same as in normally made tubes. There is, however, a tendency to higher strength as well as greater ductility at hot tensile testing of " β -treated" tubes according to the invention.

In the following text there is an example of the improved results which have been obtained by means of the new manufacturing procedure. The test included canning tubes formed from the alloy "Zircaloy 4" containing 1.2 - 1.7 percent tin, 0.18 - 0.24 percent iron, 0.07 - 0.13 percent chromium and the rest zirconium besides customary impurities. The material was prepared in the normal way by means of melting, casting, hot- and cold working up to and including the last but one cold working step. After this a division was done of the material so that one part was treated according

to the invention, whilst the other (i.e., the "reference" material) was recrystallization-annealed at 675° C., after which cold rolling with 80 percent area reduction was done. Then final annealing was performed at 500° C. The first-mentioned material was heated inductively to 1,050° C., i.e., in the β -range, for 10 seconds, after which it was air cooled to room temperature. The material was cold worked in a corresponding way (80 percent reduction) and then final annealed at 500°, 520° and 575° C. respectively.

The material prepared according to the invention and the reference material were then among other things subjected to corrosion testing and mechanical testing. Creep tests under an inside overpressure at 400° C. during certain times showed the following average values concerning the so-called transverse creep strain (the mentioned temperature values relative to final annealing):

	Material made according to the invention			Reference
	500°C	520°C	575°C	500°C
Creep strain %	0.20	0.15	0.20	1.20

The results thus show a considerable raise of the creep strength (6-8 times reduced creep strain) of the material which had been treated according to the invention.

For the rest it may be mentioned that corrosion properties, hydride orientation and texture were normal in the material which had been treated according to the invention. Hot tensile testing at 400° C. gave results of somewhat higher strength and ductility of the " β -treated" material, while the corresponding properties at room temperature were roughly equivalent.

We claim:

1. In a method of making tubes and other products with improved creep strength from a zirconium alloy containing, in Wt. percent, 1.2 - 1.7 Sn, 0.07 - 0.24 Fe, 0.05 - 0.15 Cr, 0 - 0.08 Ni, 0.09 - 0.16 O, said material having β -phase respectively α -phase structure at high respectively low temperatures, the tube or corresponding product being plastically worked to final dimension by means of hot and cold working, in which the cold working includes several steps with intermediate recrystallization annealings, the improved procedure which consists in heating the material, before the last cold working step, to the β -range and then cooling it to room temperature.

2. Method according to claim 1, wherein before the last cold working step the material is heated to a temperature between 860° - 1,250° C. and preferably to a temperature between 1,000° - 1,150° C.

3. Method according to claim 1, wherein the material after the last cold working step is annealed in the temperature range 400° - 700° C. and preferably in the temperature range 500° - 530° C.

4. Method according to claim 1, wherein the cross-sectional area of material in the last cold working step is reduced at least 50 percent.

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