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FULL NAME(S) OF APPLICANT(S)

71 FRAMATOME
COMPAGNIE GENERALE DES MATIERES NUCLEAIRES

FULL NAME(S) OF INVENTOR(S)

72 MARDON, Jean-Paul
SENEVAT, Jean
CHARQUET, Daniel

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54 ALLOY AND TUBE FOR NUCLEAR FUEL ASSEMBLY AND METHOD FOR MAKING SAME

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FOR ABSTRACT SEE THE NEXT SHEET

(54) Title: ALLOY AND TUBE FOR NUCLEAR FUEL ASSEMBLY AND METHOD FOR MAKING SAME

(54) Titre: ALLIAGE ET TUBE POUR ASSEMBLAGE DE COMBUSTIBLE NUCLEAIRE ET PROCEDE DE FABRICATION D'UN TEL TUBE

(57) **Abstract**

The invention concerns a method for making tubes designed for a nuclear fuel pencil case or guide tube which consists in forming a bar in a zirconium based alloy containing equally 0.3 to 0.25 wt. % of the total iron, of chromium or vanadium, 0.8 to 1.3 wt. % of niobium, less than 2000 ppm of tin, 500 to 2000 ppm of oxygen, less than 100 ppm of carbon, 5 to 30 ppm of sulphur and less than 50 ppm of silicon. The bar is soaked in water after being heated at a temperature between 1000 °C and 1200 °C. A blank is spun after being heated at a temperature between 600 °C and 800 °C. The blank is cold–rolled, in at least three of four passes, to obtain a tube with intermediate heat treatments between 560 °C and 620 °C and s final heat treatment is carried out between 560 °C and 620 °C in inert atmosphere or under vacuum.

(57) **Abrégé**

Pour fabriquer des tubes destinés à une gaine de crayon de combustible nucléaire ou un tube guide, on constitue une barre en un alliage à base de zirconium contenant également en poids, 0,03 à 0,25 % au total de fer d'une part, de chrome ou de vanadium d'autre part, 0,8 à 1,3 % en poids de niobium, moins de 2000 ppm d'étain, 500 à 2000 ppm d'oxygène, moins de 100 ppm de carbone, de 5 à 30 ppm de soufre et moins de 50 ppm de silicium. On trempe à l'eau la barre après chauffage entre 1000 °C et 1200 °C. On file une ébauche après chauffage de 600 °C à 800 °C. On lamine l'ébauche à froid, en au moins quatre passes, pour obtenir un tube, avec des traitements thermiques intermédiaires entre 560 °C et 620 °C et on effectue un traitement thermique final entre 560 °C et 620 °C, en atmosphère inerte ou sous vide.

ALLOY AND TUBE FOR NUCLEAR FUEL ASSEMBLY AND METHOD FOR MAKING SAME

The present invention relates to tubes made from an alloy with a zirconium base intended for making all or the external part of the sheath of a nuclear fuel rod or a guide tube as well as the alloys used to make such tubes. One important although not exclusive application is the manufacture of sheathing tubes for fuel rods designed for those of light water reactors and in particular pressurized water reactors in which the risks of corrosion are particularly high due to a high lithium content and/or risks of boiling.

A method of manufacturing tubes enabling a high resistance to corrosion and a satisfactory capacity to withstand creep has already been proposed (FR A-2 729 000 or EP 720 177), starting with an ingot of a zirconium based alloy which also contains 50 to 250 ppm of iron, 0.8 to 1.3% by weight of niobium, less than 1600 ppm of oxygen, less than 200 ppm of carbon and less than 120 ppm of silicon.

An object of this invention is to provide an alloy and a method of manufacturing tubes which are even more resistant to corrosion and whose composition will not hamper the rolling stages of manufacture.

To this end, the invention proposes in particular an alloy with a zirconium base which also contains, by weight, other than the inevitable impurities, 0.03 to 0.25% in total firstly of iron, secondly of at least one

of the elements from the group comprising chromium and vanadium, with 0.8 to 1.3% of niobium, less than 2000 ppm of tin, 500 to 2000 ppm of oxygen, less than 100 ppm of carbon, 5 to 35 ppm of sulfur and less than 50 ppm of silicon, the ratio between the iron content firstly and the chromium or vanadium content secondly ranging between 0.5 and 30.

If it has a low content of iron, chromium, vanadium and tin, an alloy of this type can also be used to make grill plates for a nuclear fuel assembly.

The invention also proposes a casing tube for a nuclear fuel rod or guide tube for a fuel assembly made from an alloy with a zirconium base, also containing, by weight, 0.03 to 0.25% in total of, firstly iron, secondly, at least one of the elements from the group comprising chromium and vanadium, 0.8 to 1.3% by weight of niobium, less than 2000 ppm of tin, 500 to 2000 ppm of oxygen, less than 100 ppm of carbon, 5 to 35 ppm of sulfur and less than 50 ppm of silicon, in the re-crystallized state, at least the greater part of the iron therein being in the form of $Zr(Nb,Fe,Cr)_2$ or $Zr(Nb,Fe,V)_2$.

The invention also proposes a manufacturing method, comprising :

- forming a bar of a zirconium based alloy which also contains, other than the inevitable impurities, 0.03 to 0.25% in total firstly of iron, secondly, of at least one of the elements from the group comprising chromium and vanadium, having 0.8 to 1.3% of niobium, less than

2000 ppm of tin, 500 to 2000 ppm of oxygen, less than 100 ppm of carbon, 5 to 35 ppm of sulfur and less than 50 ppm of silicon, the ratio between firstly the iron content and secondly the chromium or vanadium content ranging between 0.5 and 30,

- quenching the bar in water after heating to between 1000°C and 1200°C,

- extruding a blank after heating to a temperature of between 600°C and 800°C,

- cold rolling said blank in at least four passes to obtain a tube, with intermediate heat treatments between 560°C and 620°C, and

- applying a final heat treatment at between 560°C and 620°C, all heat treatments being applied in an inert atmosphere or under vacuum.

The final heat treatment brings the tube to the re-crystallized state without modifying the nature of the phases.

An oxygen content ranging between 1000 and 1600 ppm is of particular advantage. It may be adjusted by deliberate and controlled addition of zirconia before casting.

More often than not, an alloy without vanadium will be used. However, vanadium may replace some of the chromium for a high Fe/Cr ratio or even all.

In alloys containing approximately 1% of Nb, the presence of iron with a content in excess of 75 ppm and chromium and/or vanadium in a content in excess of 5 ppm

produces iron contents of not more than 0.20% with intermetallic compounds of the type $Zr(Nb, Fe, Cr)_2$ or $Zr(Nb,Fe,V)_2$. Chromium is always present to form such compounds if contained in the alloy in a quantity of more than 5 ppm. The existence of the intermetallic compound reduces the quantity of β phase niobium precipitates and also reduces the niobium content in solid solution.

The above-mentioned intermetallic compounds, which constitute a Laves phase, precipitate in a very fine form, with a size of between 100 and 200 nanometers. They substitute to the precipitates of phase β niobium. They significantly improve the resistance in a lithium-containing medium without significantly affecting the uniform resistance to corrosion at a temperature of 400°C, representative of the temperature prevailing in reactors.

It is preferable not to exceed a total Fe+(Cr and/or V) content of 2500 ppm (i.e. 0.25% by weight), even though higher contents remain beneficial in terms of resistance to corrosion in a lithium-containing medium. The reason for this is that, in addition to the Laves phase, a precipitate of the type $(Zr, Nb)_4Fe_2$ appears, the diameter of which can be as much as 1 μm and which is detrimental from the point of view of rollability. A maximum content of 0.20% constitutes a compromise close to optimum between corrosion in a lithium-containing medium and rollability.

The presence of chromium in the intermetallic precipitates of type $Zr (Nb, Fe, Cr)_2$ does not have any marked effect on corrosion at 400°C up to a Fe/Cr ratio

of about 30 because in this range, chromium is simply substituted for iron in the intermetallic precipitates as the chromium content increases. The Fe content may be limited to 0.20% to avoid that excess iron causes too high a content in the $(Zr, Nb)_4Fe_2$ phase. Improved resistance to corrosion at 400°C is obtained if the Fe/(Cr+V) ratio is higher than 0.5 and the sum of Fe+Cr+V is at least 0.03%.

Table I below illustrates how the iron content affects the corrosion behavior of a sample of zirconium alloy with 1% of niobium for different iron contents:

TABLE I

Fe ppm	Mass increase (mg/dm^2)	
	lithium-containing water with 70 ppm Li	steam phase
	360°C - 28 days (with pre-filming)	400°C - 262 days
120	2070	240
1480	1670	250
2920	315	240
4300	25	270

The contents of C, Si, S, O_2 and Sn were essentially identical for all samples and were below the maximum values given above; they were less than 300 ppm for tin.

Pre-filming is an operation intended to accelerate the response and selectivity of the corrosion test ; this operation makes it possible to determine the effect of additives on corrosion more rapidly.

The sample was manufactured by thermo-metallurgical operations comparable to those given above, i.e. not exceeding a temperature of 620°C.

The effect of the Fe/Cr ratio in the precipitates is shown in table 2 below, which gives the increase in weight of alloy samples after being kept in steam for 200 days at a temperature of 400°C. It may be noted that the variation due to change of Fe/Cr is relatively low.

TABLE II

Fe/Cr in the precipitates	Gain in weight mg/dm^2
0.5	100
1	110
2	120
5	110
30	100

Complementary tests have shown that similar results are obtained if the chromium is replaced by vanadium. The chromium or vanadium contents are selected so as to be low enough not to cause any major difficulties during the metallurgical treatments and in particular rolling.

At present, the lithium content in the water in pressurized water reactors is not more than a few ppm. This being the case, it is of advantage to keep the tin content to less than 300 ppm. A higher content has a slightly adverse affect on resistance to uniform corrosion in water steam at about 415°C (whereas its effect on nodular corrosion in steam at 500°C is negligible).

On the other hand, incorporating tin in a quantity of between 300 and 2000 ppm and in particular between 1000 and 1500 ppm considerably reduces corrosion in an aqueous medium with the levels of lithium content currently used to run reactors. Above 1500 ppm, resistance in the lithium-containing medium is only slightly improved by increasing the tin content so that there would rarely be any point in going above a value of 1500 ppm of tin.

The effects described above are set out in Table III below:

TABLE III - Corrosion in autoclave

Tin content as a %	Mass gain (mg/dm^2)		
	Steam 1 day at 500°C	Steam 105 days at 415°C	mass gain in water with 70 ppm lithium after 28 days at 360°C, with pre-heating in steam
0.00	37	135	2560
0.05	43	141	2270
0.10	43	155	1200
0.15	42	165	580
0.25	44	173	280

The tests set out in table III, the purpose of which was to ascertain the effect of tin, were conducted on an alloy with a 1% Nb content, iron, chromium and vanadium being present only as impurities. They demonstrate an unexpectedly favorable effect of tin in a lithium-containing medium without any unacceptable degradation as regards corrosion in steam.

The contents of C, Si, S, O_2 and Sn were substantially identical for all samples and were below the maximum values given above.

CLAIMS

1. Zirconium based alloy also containing, by weight, 0.03 to 0.25% in total firstly of iron and secondly at least one of the elements from the group comprising chromium and vanadium, 0.8% to 1.3% by weight of niobium, less than 2000 ppm of tin, 500 to 2000 ppm of oxygen, less than 100 ppm of carbon, 5 to 35 ppm of sulfur and less than 50 ppm of silicon.

2. Sheathing tube for a nuclear fuel rod or guide tube for a nuclear fuel assembly, made from a zirconium based alloy also containing, by weight, 0.03 to 0.25% in total firstly of iron and secondly at least one of the elements from the group comprising chromium and vanadium, 0.8% to 1.3% by weight of niobium, less than 2000 ppm of tin, 500 to 2000 ppm of oxygen, less than 100 ppm of carbon, 5 to 35 ppm of sulfur and less than 50 ppm of silicon, in the re-crystallized state, at least the greater part of the iron being in the form $Zr(Nb,Fe,Cr)_2$ or $Zr(Nb,Fe,V)_2$ and in which the intermetallic compounds are of a size not exceeding 200 nm.

3. Tube as claimed in claim 2, characterized in that the oxygen content is between 1000 and 1600 ppm.

4. Tube as claimed in claim 2 or 3, characterized in that the content of tin is less than 300 ppm.

5. Tube as claimed in claim 2 or 3, characterized in that the content of tin is between 300 and 1500 ppm.

6. Sheet of alloy as claimed in claim 1.

7. Method of manufacturing tubes intended for making all or the external part of a sheathing tube for a

nuclear fuel rod or a guide tube for a nuclear fuel assembly, characterized in that a bar is formed of a zirconium based alloy which also contains, firstly 0.03 to 0.25% in total firstly of iron, secondly, at least one of the elements from the group comprising chromium and vanadium, 0.8 to 1.3% of niobium, less than 2000 ppm of tin, 500 to 2000 ppm of oxygen, less than 100 ppm of carbon, 5 to 35 ppm of sulfur and less than 50 ppm of silicon,

- quenching the bar in water after heating to between 1000° and 1200°C,

- extruding a blank after heating to a temperature of between 600°C and 800°C,

- cold-rolling said blank in at least four passes to obtain a tube, with intermediate heat treatments between 560°C and 620°C, and

- applying a final heat treatment at between 560°C and 620°C, all the heat treatments being applied in an inert atmosphere or under vacuum.

8. Method as claimed in claim 7, characterized in that the alloy contains at most 0.20% of iron.

9. Method as claimed in claim 7, characterized in that the Fe/(Cr+V) ratio is between 0.5 and 30 by weight.

10. Method as claimed in claim 7, characterized in that the Fe/(Cr+V) ratio is at least 0.5 and the content of Fe+Cr+V is at least 0.03%.

11. Method as claimed in any one of claims 7 to 10, characterized in that the oxygen content is between 1000 and 1600 ppm.