Sept. 12, 1967 E. W. EVANS ET AL 3,341,373

METHOD OF TREATING ZIRCONIUM-BASE ALLOYS

Filed Sept. 25, 1963 2 Sheets-Sheet 1

MATERIAL β ROLLED (1,000°C), COLD ROLLED 50%, SOLUTION TREATED 825°C, W.Q. COLD ROLLED 30% AND AGED.

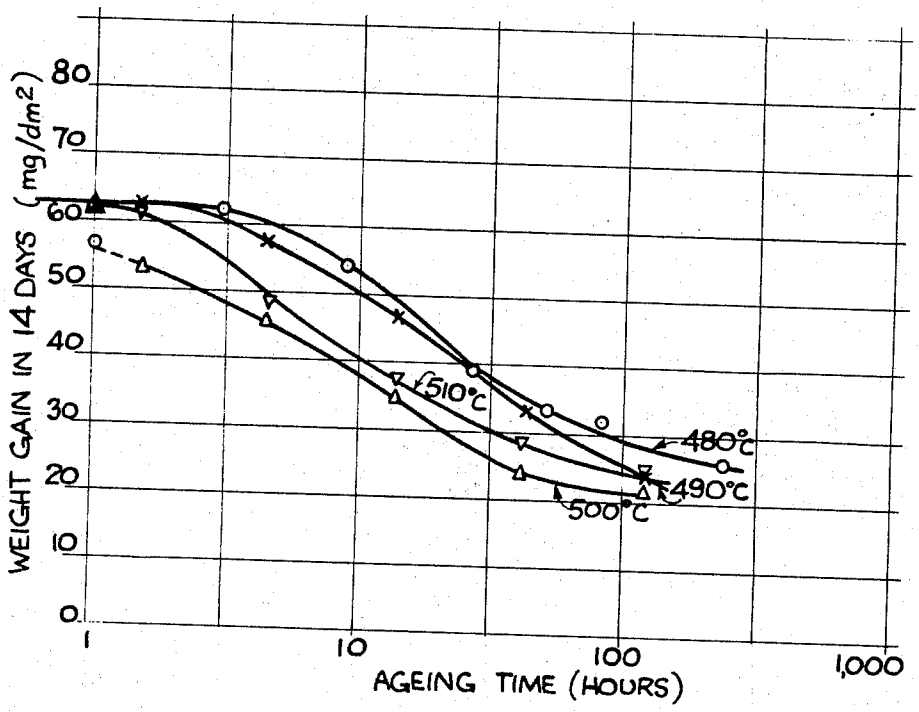


FIG. 1.

INVENTORS
EVAN WILLIAM EVANS
DONALD GRAINGER LEES
By Cushman, Darby & Cushman
ATTORNEYS

Sept. 12, 1967 E. W. EVANS ET AL 3,341,373

METHOD OF TREATING ZIRCONIUM-BASE ALLOYS

Filed Sept. 25, 1963

2 Sheets-Sheet 2

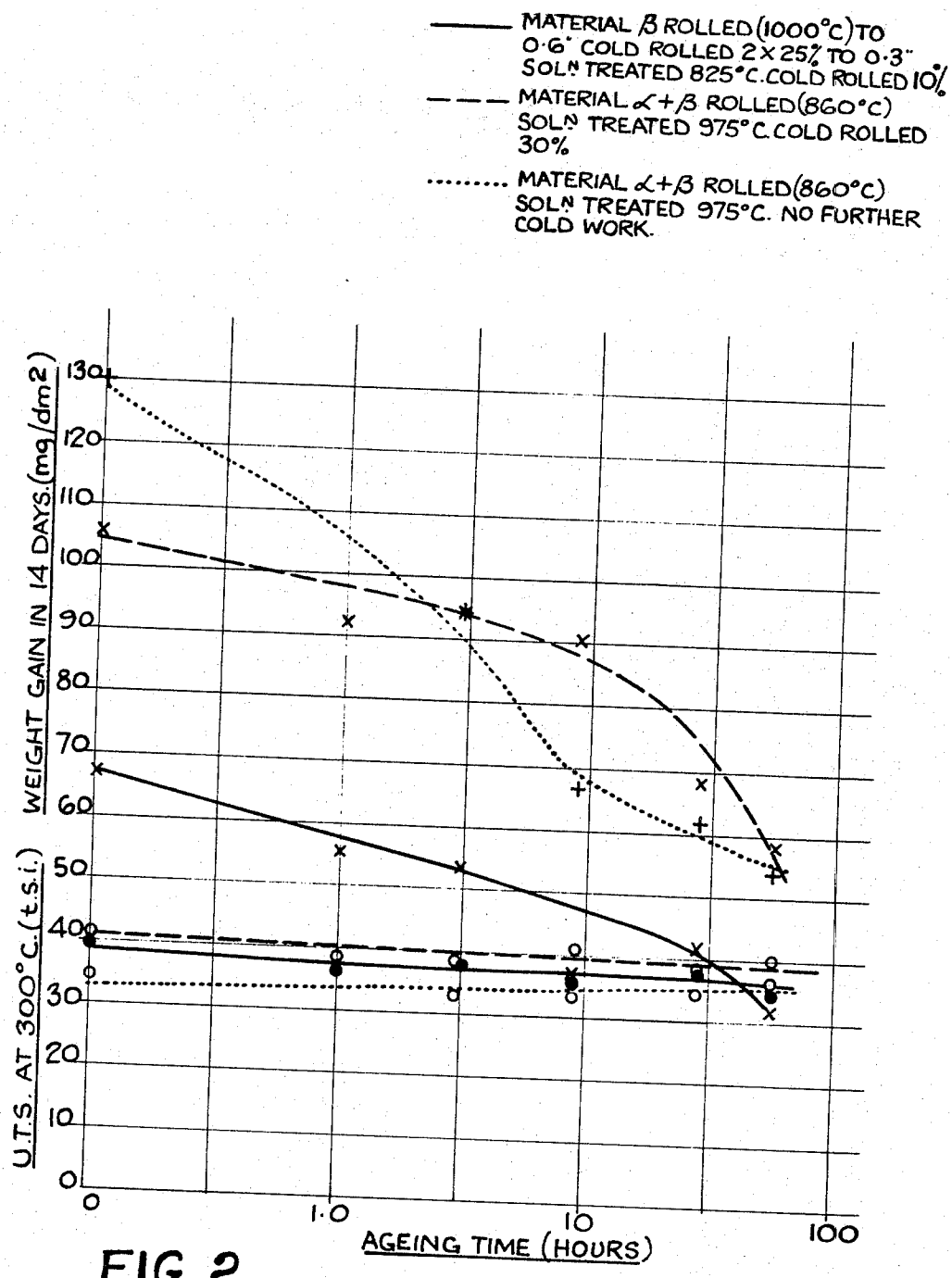


FIG. 2

INVENTORS
EVAN WILLIAM EVANS
DONALD GRAINGER LEES
By Cushman, Darby & Cushman
ATTORNEYS

United States Patent Office 3,341,373 Patented Sept. 12, 1967

3,341,373

METHOD OF TREATING ZIRCONIUM-BASE ALLOYS

Evan William Evans, Hagley, and Donald Grainger Lees, Redditch, England, assignors to Imperial Metal Industries (Kynock) Limited, London, England, a corporation of Great Britain

Filed Sept. 25, 1963, Ser. No. 311,531
Claims priority, application Great Britain, Sept. 26, 1962, 36,583/62
9 Claims. (Cl. 148—12.7)

The invention relates to zirconium-base alloys.

The zirconium-2½% niobium alloy has good creep strength and low rate of hydrogen absorption compared with the alloy known as Zircaloy 2 which contains nominally 1.5% tin, 0.15% iron, 0.1% chromium and 0.05% nickel. The 2½% niobium alloy is potentially useful for application in water-cooled nuclear reactors but has limited corrosion resistance when in the solution-treated and aged condition and the present invention is concerned with a method of treating the alloy whereby good strength is maintained with considerable improvement in corrosion resistance.

According to the invention a method of heat-treating an alloy consisting of 2–3% niobium, balance zirconium apart from usual impurities, includes the steps of cold working the alloy up to approximately 50% reduction, solution-treating at a temperature above the alpha/alpha plus beta transition temperature, cold-working a second time to a reduction between approximately 10% and 50% and ageing at a temperature between 470 and 520° C.

Preferably the alloy is solution-treated at 825° C., but a range of 800 to 860° C. can be used to obtain maximum corrosion resistance. Higher tensile strengths can be obtained by solution-treating at higher temperatures followed by ageing with somewhat lower but still improved corrosion resistance.

In the solution-treating step the alloy is oil quenched or water quenched. The step of quenching is included in the term "solution-treated" in this specification and its claims.

Strength in the aged condition depends on rolling temperature and on solution-treatment temperature. Cold-rolled material subsequently solution-treated has higher tensile strength than material hot-rolled and solution-treated. There is also an increase in strength brought about by cold-working after solution-treatment and this seems to be independent of the solution-treatment temperature. In both cases there is some loss of ductility.

Cold-working after solution-treatment considerably improves corrosion resistance and effects a very marked reduction in the amount of hydrogen which is picked up during prolonged exposure to steam. A cold-working reduction of 30% has been found to produce good corrosion resistance. In preparation for the first cold-rolling operation, the alloy may be reduced to a suitably sized work-piece by hot-forging at about 950° C. and hot-rolling at about 1000° C.

The ageing temperature may be in the range 470°–520° C. and the optimum range is 480°–510° C. By the use of a temperature high in the range, the ageing time can be shortened, but if the upper limit of the range is exceeded, for any duration of ageing, there is an increase in corrosion rate. During ageing, niobium solid solution is precipitated, but the hardening effect is balanced more or less by softening due to recovery.

In FIGURE 1 of the accompanying drawings is shown a series of curves which demonstrate that the optimum ageing temperatures are found in the range 480°–510° C. It will be seen that 500° C. produces the best corrosion resistance and that 480°, 490° and 510° C. give

slightly higher corrosion rates. Ageing temperatures above and below this range produce a further increase in corrosion rate.

In the fully annealed condition, zirconium-2½% niobium alloy has a strength of about 40 tons/sq. in. at room temperature and about 23 tons/sq. in. at 300° C. By treatment in accordance with the invention, it is possible to raise its strength at 300° C. to at least 35 and possibly to 40 tons/sq. in.

The following is an example of the treatment of a zirconium-2½% niobium alloy.

After rolling at 1000° C. to 0.6 inch thickness, a specimen was cold-rolled to 50% reduction with an anneal at 25% reduction and solution-treated at 825° C. The specimen was then cold-rolled to 10% reduction and aged at 480° C. Corrosion tests in steam at 400° C. and at 1500 lbs./sq. in. pressure and elevated temperature tensile tests were carried out and are recorded in the table below.

TABLE.—10% REDUCTION

Ageing time (hours)	14-day weight gain (mg./dm.²)	U.T.S. at 300° C. (tons/sq. in.)
0	68	40.1
1	55	37.6
3	53	38.4
9	37	35.9
27	41	37.5
51	32	35.3

The above values are compared in FIGURE 2 of the accompanying drawings with those for material of the same composition treated at different solution-treatment temperatures and omitting one or both cold-working steps. In the drawing the variation of ultimate tensile strength at 300° C. and corrosion resistance expressed as weight gain in steam at 400° C. and 1500 lbs./sq. in. are plotted against time of ageing at 480° C. It will be seen that the lower solution-treatment temperature, 825° C., yields material of moderate corrosion rate, 68 mg./dm.², which improves to 32 mg./dm.² on ageing to 51 hours. Over this period of ageing there is only a small loss of strength of approximately 5 tons/sq. in. from 40 to 35 tons/sq. in. Whilst similar behaviour is shown by material solution-treated at 975° C. and cold-rolled, corrosion resistance is poorer in the as solution-treated condition and starts to improve rapidly only after ageing for 10 hours. After 51 hours, the strength at 38 tons/sq. in. is 3 tons/sq. in. higher than for the material solution-treated at 825° C., but the corrosion rate is almost twice as high, 58.5 mg./dm.² compared with 33 mg./dm.². The decrease in corrosion resistance is clearly shown in the second set of curves of FIGURE 2. The third set of curves in FIGURE 2 refer to material which was solution-treated at 975° C., but not cold-worked before ageing at 480° C. It will be seen that there is a small increase in strength, but the corrosion rate at 51 hours is still twice that of the alloy treated in accordance with the invention.

Tests on the alloy treated in accordance with the invention show that the resistance to corrosion by carbon-dioxide at 300° and 400° C. follows the same pattern as the improvement to corrosion in steam at 400° C.

The invention is important in the manufacture of tubes for use in water-cooled nuclear reactors in that it produces not only a combination of superior tensile properties and corrosion resistance, but provides a processing schedule that allows straightening of the tubes after solution-treatment and before ageing and so minimises the effect of distortion resulting from quenching.

We claim:

1. A method of heat-treating an alloy consisting of 2–3% niobium, balance zirconium apart from usual impurities includes the steps of cold-working the alloy up

to 50% reduction approximately, solution-treating at a temperature above the alpha/alpha plus beta transition temperature, cold-working a second time to a reduction between approximately 10% and 50% reduction and ageing at a temperature between 470°–520° C.

2. A method of heat-treating an alloy as claimed in claim 1 in which the solution-treatment temperature is in the range 800° to 860° C.

3. A method of heat-treating an alloy as claimed in claim 1 in which the solution-treatment temperature is 825° C.

4. A method of heat-treating an alloy as claimed in claim 1 in which the ageing temperature is in the range 480° to 510° C.

5. A method of heat-treating an alloy as claimed in claim 1 in which the ageing temperature is 500° C.

6. A method of heat-treating an alloy as claimed in claim 1 in which the alloy is reduced 50% in the first mentioned cold-rolling step.

7. A method of heat-treating an alloy as claimed in claim 1 in which the alloy is reduced 30% in the second mentioned cold-rolling step.

8. A method of heat-treating an alloy consisting of 2½% niobium, balance zirconium apart from impurities, which comprises cold-rolling to 50% reduction in two stages of 25% reduction with annealing between the stages, solution-treating at 825° C., cold-rolling to 10% reduction and ageing at 480° C.

9. A method of producing tube from an alloy consisting of 2–3% niobium, balance zirconium apart from impurities, which includes the steps of cold-rolling to a reduction of up to approximately 50%, solution-treating by heating to a temperature above the alpha/alpha plus beta transition temperature and cooling rapidly, removing distortion from the tube, cold-working a second time to a reduction between approximately 10% and 50% and ageing at a temperature between 470° and 520° C.

References Cited

UNITED STATES PATENTS

2,894,866	7/1959	Picklesimer	148—11.5
3,121,034	2/1964	Anderko et al.	148—11.5
3,205,070	9/1965	Bertea et al.	75—177

DAVID L. RECK, *Primary Examiner.*

HYLAND BIZOT, *Examiner.*

H. F. SAITO, *Assistant Examiner.*