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ALUMINUM ALLOYS RECRYSTALLIZING AT LOWER TEMPERATURE

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This invention relates to a method of treating aluminum and aluminum alloys to give the improved low temperature softening properties.

With respect to metals hardened by working, when these metals heated to a temperature above a certain degree, there occurs the so-called recrystallization effect to relieve the working strain and create fresh crystalline grains so as to soften the metals. The recrystallization temperature which is the temperature at which recrystallization occurs depends on the purity of the metal, degree of final working and heating time, but the recrystallization temperature of aluminum which is generally used at pressent is about 250 to 350° C.

It is sometimes desirable that aluminum alloys be softened naturally at a temperature lower than 250° C. and preferably at room temperature without any special heat-treatment after they have been worked.

Heretofore no such aluminum alloys have been available for industrial purposes even though it is known that when aluminum of 99.99% purity added thereto more than 0.48% of calcium then the alloy recrystallizes at a fairly low temperature (150° C. for 1 hour) and also if aluminum of lower purity has 0.04 to 1.0% of nickel and 0.05 to 0.25% of Be added thereto, then the alloy undergoes recrystallization at 200° C. But, it is impossible to soften the Ni-and Be-containing aluminum below 200° C., and it has been considered difficult to lower the recrystallization temperature for aluminum of 99.99% purity if provided with less than 0.48% of calcium and aluminum of less than 99.99% purity by adding calcium.

I have found that aluminum alloys which will soften at lower temperature can be obtained when even less than 0.48% of calcium is added to aluminum of higher than 99.99% purity and also when a proper amount of calcium is added to aluminum of less than 99.99% purity if these aluminums are subjected to heat-treatment and severe working.

Thus the present invention proposes that aluminum and its alloys, to which are added calcium of 0.001 to 0.47%, be heated at a temperature of from 150° C. to 500° C. and subsequently subjected to cold working to produce more than 30% reduction in cross sectional area, thereby providing aluminum alloys which recrystallize at a lower temperature.

In general, if some other element is added to aluminum the temperature at which the alloy recrystallizes becomes higher. On the other hand, according to this invention, in spite of the addition of calcium to aluminum by subjecting the aluminum alloy to further heat-treatment and working, an aluminum alloy which recrystallizes at lower temperature, or an aluminum alloy which completes recrystallization with heating for a shorter time can be obtained.

According to this invention, heat-treatment is indispensable for giving the improved recrystallization property at lower temperature to the aluminum alloy, and the range of effective heat-treatment depends on the purity

of aluminum and generally increases as the purity increases.

Through addition of calcium and subjecting to proper heat-treatments impurities which have raised the recrystallization temperature of aluminum are precipitated from the solid solution and the aluminum matrix is perfectly purified and the aluminum thus purified can be softened at room temperature just like super-pure aluminum recrystallizes even below 0° C. Therefore, the range of necessary heat-treatments which are effective to purify the matrix perfectly changes widely according to the kinds of impurities and their quantity contained in aluminum. For instance, the recrystallization temperature of hard worked 99.99% Al—0.45% Ca alloy is lowered widely if it is heated at intermediate heat-treatment to a temperature of from 200 to 500° C. for one hour, or even one minute holding at 500° C., but that of 99.7% Al—0.3% Ca alloy can never be lowered even by any prolonged intermediate heating at 200 or 500° C.

Thus, it should be understood that it is impossible to specify precisely the condition of effective heat-treatments, case by case, covering all the alloys, in which purity of aluminum and calcium content are so varied.

Moreover, comparatively severe final cold working is necessary for further improving the low temperature recrystallization obtained by the addition of calcium and heat-treatment, and the larger the degree of working the greater the effect becomes. In the present invention, the addition of calcium is limited to 0.001 to 0.47% owing to the reason that there is no effect when the amount of calcium added is below 0.001%, and at more than 0.47% the alloy becomes harder and more corrosive. As, even at 0.47% the alloy recrystallizes at room temperature, the maximum quantity is limited to 0.47% in order to maintain the characteristics of pure aluminum. Further, in this invention, the reason why the temperature of heat-treatment is selected to be a temperature of from 150 to 500° C., and the reason for having the final degree of working to over 30%, are that some effects could be observed even outside these ranges in some cases, although remarkable effects could not be obtained. The final working can be applied more than 99% in case of foils, and generally, the higher the rate of cold working the greater the effect becomes but such effect is not so remarkable when the degree of working is below 30%.

In carrying out the present invention, use is made of aluminum having purities of 99.99%, 99.9%, 99.7%, 99.5%, which are most suitable, but impurities and additional matters may be contained to the maximum each of 4.0% of Fe, 3.0% of Si, 0.6% of Cu, 0.1% of Mg, 0.1% of Mn, 0.08% of Cr, 0.1% of Ti, 6.0% of Zn, 4.0% of Ni, 1.0% of Be, 2.0% of B, 4.0% of Sn and less than 0.1% each of Mo, V, and Zr.

Examples of this invention are given below:

Ingots of aluminum to which different amounts of calcium are added, are subjected to hot or cold working and also to the final working with or without heat-treatment at suitable stages, and subsequently cold worked to finished plates of 0.1 mm. in thickness. The comparison of the conditions of treatment and the recrystallization temperatures of the finished plates with those of the samples not subjected to the treatment of this invention are shown in the following table:

Here, the recrystallization temperature indicates the

temperature at which softening has been completed by heating for 30 minutes.

No.	Aluminum, percent	Added calcium, percent	Heat-treatment	Final working, percent	Recrystallization temp., ° C.
1	99.99	0	A	95	250.
2	99.99	0.004	no	95	250.
3	99.99	0.004	A	95	150.
4	99.99	0.2	no	95	300.
5	99.99	0.2	A	20	300.
6	99.99	0.2	A	40	100.
7	99.99	0.2	A	95	room temp.
8	99.7	0.4	no	95	325.
9	99.7	0.4	250° C x 5 Hr.	95	room temp.
10	99.7	0.4	B	95	125.
11	99.7	0.4	C	95	room temp.
12	99.3	2.0	C	95	100.
13	99.99+Fe, 3.0%	1.0	C	95	room temp.
14	99.99+Si, 2.0%	1.7	C	95	50.
15	99.8+Cu, 0.4%	2.0	C	95	100.
16	99.8+Mg, 0.05%	2.0	C	95	150.
17	99.8+Mn, 0.05%	2.0	C	95	125.
18	99.99+Cr, 0.04%	1.0	C	95	room temp.
19	99.99+Ti, 0.07%	1.0	C	95	Do.
20	99.99+Zn, 4.0%	2.0	C	95	50.
21	99.99+Ni, 3.0%	1.0	C	95	room temp.
22	99.99+Be, 0.5%	1.0	C	95	Do.
23	99.99+B, 1.0%	1.0	C	95	Do.
24	99.99+Sn, 2.0%	1.0	C	95	Do.

A represents heat-treatment by heating at 500° C. for 10 hours, and afterwards cooling from 500 to 250° C. at the rate of 30° C. per hour.

B represents heat-treatment by cooling from 500 to 200° C. at the rate of 250° C. per hour.

C represents heat-treatments in which cold work was done after A, and then the alloys were heated at 250° C. for 10 hours.

In the above table, samples numbered 1, 2, 4, 5 and 8 are those to which no part of this invention was applied. As can be observed from the above table, when the same quantity of calcium is added to the same base aluminum metal, those subjected to the treatment of this invention showed lowering of recrystallization temperature, and the one which recrystallized at a remarkably low temperature recrystallized at room temperature. Aluminum of lower purity such as in Nos. 12–14, 20, 21, 23 and 24 showed recrystallization at sufficiently low temperature.

On the contrary, in Samples Nos. 2, 4, 5 and 8, to which even if calcium was added, heat-treatment or working, according to this invention, was not applied thereto, no lowering of temperature of recrystallization was found.

The aluminum alloys of this invention become not only softened at a lower temperature and provide fine recrystallized grains, but also show improvements in corrosion resistance and electric conductivity compared with base aluminum metals and aluminum alloys with mere addition of calcium, and not subjected to heat-treatment of this invention as the matrix of aluminum treated by the method of this invention has been purified perfectly. For instance, the electric conductivities of three kinds of aluminum wires, that of 99.7% purity, that to which is added 0.07% of calcium, and that subjected to the heat-treatment according to this invention after the same aluminum 0.07% of calcium added thereto, were 62.2%, 62.5% and 62.9% respectively. Moreover, the perfectly softened material become softer. For

instance, the tensile strengths when the aluminum of 99.7% purity, and aluminum alloy of the same purity to which is added 0.2% of calcium, and made to plates processed by the same process were 7.0 kg./mm.^{2} and 5.8 kg./mm.^{2} respectively. Further, aluminum alloys, in general, are likely to be stained by the burning of oil used in case of annealing, but the alloys of this invention have no such troubles since the alloy softens at a lower temperature.

The aluminum alloys of this invention can be very effectively used for foils, cable sheaths, extruding materials, impact extrusion materials, deep drawing materials and corrosion resisting materials and electric conductors. When used for foils the present alloy shows small degree of work-hardening and can be softened at a lower temperature, and if a suitable method of manufacturing is adopted, it needs no other intermediate or final annealing besides the heat-treatment according to this invention. Also splendid foils can be obtained without pin holes and with fine recrystallized grains.

When the aluminum alloy of this invention is used for the sheathing material in cables for electric power transmission and communication, softened aluminum sheaths can be provided on the cable at a low extruding temperature without deteriorating the cable insulation. Moreover, by directly extruding the aluminum alloy onto the cable at room temperature, annealing after sheathing is unnecessary or may be effected at a lower temperature.

What I claim is:

1. A process of treating aluminum comprising adding 0.001 to 0.47% of calcium to the aluminum, heating said aluminum to a temperature between about 250° to 500° C. for at least ten hours, gradually cooling said aluminum to a temperature between 150° C. and its recrystallization temperature and cold working the aluminum to produce more than a 30% reduction in the cross sectional area.

2. A process of treating aluminum to make the same softer, have greater corrosion resistance, higher electrical conductivity and a lower recrystallization temperature as compared to calcium free aluminum, and aluminum containing calcium, but not subjected to heat treatment and working, the process comprising adding 0.001 to 0.47% of calcium to the aluminum, heating said aluminum to a temperature of 500° C. for at least 10 hours, gradually cooling said aluminum to a temperature between 150° C. and its recrystallization temperature for at least 5 hours, and cold working the aluminum to produce more than a 30% reduction in its cross sectional area.

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