## ALIEN PROPERTY CUSTODIAN

LIGHT AND ULTRA-LIGHT ALLOYS AND THE METHODS OF THEIR MANUFACTURE

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Our invention relates to ultra-light alloys containing aluminium and magnesium, the proportion of magnesium being greater than 50%. More particularly it relates to aluminium-magnesium base alloys and a method of making the same whereby certain desirable properties in such alloys are assured. This application is a third continuation-in-part of our application Serial No. 150,880, filed June 28, 1937; a first continuation-in-part having been filed June 19th, 1939, 10 with Serial No. 279,992, and a second continuation-in-part May 13th, 1940, with Serial No. 334,986.

The principal object of the invention resides surface of the alloy which guards the alloy from corrosion in sea water and the like. This film has the remarkable capacity of cicatrizing. That is, if the film is fractured or broken, this fracture is immediately closed up or "healed" by the 20 automatic formation of a protective scar.

Ordinary aluminium-magnesium base alloys heretofore known do not possess this remarkable property. While some of the literature has given which are resistant to corrosion, no example has been disclosed of an alloy having a self-healing protective film, and no disclosure, of which we are aware, has in any way taught how an alloy having such a remarkable property can be produced particularly with any degree of assurance.

The invention is based on a remarkable discovery we have made after many experiments and is based on a new principle.

According to this new principle and discovery, 35 ject desired. an alloy is formed of aluminium and magnesium, and by utilizing predetermined proportions of these base metals, and by adding one or more other metals which meet very rigid requirements as to amounts and properties, there is automatically formed on the surface of the alloy a uniform: adherent, leak-proof, protective film which possesses the astounding property of cicartrizing (forming a scar, healing, closing up) immediately after fracture.

It is consequently the principal object of our invention to provide such an alloy and a method whereby it may be produced, not haphazardly and perchance occasionally, but every time the distates of the following specification are followed.

A more specific object of the invention is the provision of an alloy having a self-protective and self-healing film and having a finely heterogeneous, approximately eutectic structure which, when certain requisites of the invention are car-

ried out, results in the formation of a multitude of galvanic couples. These galvanic couples, being tinely distributed, assure the rapid formation of the protective film in the presence of a nor-5 maily corrosive agent such as sea water.

As already indicated the results desired can only be obtained by rigidly observing certain requisites. Particularly these requisites will now be described.

The alloy has a base of aluminium and magnesium. These base metals should be employed only in an extremely pure state. Impurities should be avoided and in any case should be less than 0.10%. This is particularly so of iron and in the provision of a self-protecting film on the 15 silicon whose presence is exceptionally undesirable and even fatal to the results desired.

The proportion of magnesium can be chosen between 50% and 99%. It has been found that the best proportions are comprised between 85% and 96% preferably 90%.

An alloy containing only aluminium and magnesium, even with the proportions given above, will not give the results of the present invention. In addition to these metals, in the proportions examples of aluminium-magnesium base alloys 25 set forth, we have found that the invention can only be carried out by carefully selecting and adding an additional metal or metals in accordance with specific requirements.

The additional metal must first of all be easily oxidizable.

Secondly, the additional metal should be more precious than the base metals. Any other metal not responding to these conditions should be exe'uded as an impurity inconsistent with the ob-

The oxidizing property of the addition metal acts primarily in the electrolytic formation of unattackable oxides or oxychlorides, which make up the protective self-healing film. This, how-40 ever, is only produced by galvanic couples formed between the addition metal and the base metals and in which the ions are displaced from the particles of the addition metal by the base metal. Hence, the requirement that the addition metal 45 should be more precious than the base metals aluminium and magnesium.

When mention is made herein of metals which are more precious than the base metals, reference is had to the electromotive series which lists the 50 metals with respect to their axtivity, that is, the ease with which they give up electrons. In general, as is well known, each metal displaces the ions of those which follow it in the list.

Another requirement of the addition metal is that it must be capable of forming a eutectic with at least one of the base metals and should be present in an amount which preferably will approximate the amount which will form a eutectic with the base metals. This contributes to assure a fine distribution of the metals and gives rise to a great number of elementary piles 5 between which electrolytic action is exerted to a maximum when the alloy is exposed to the action of a corrosive agent such as salt water.

The term eutectic is a definite term known to those skilled in metallurgy. The kinds of metals 10 lows: and the amounts thereof which will form a eutectic with another metal can, of course, be determined from phase diagrams in the technical literature.

When we say that the addition metal should 15 be capable of forming a eutectic mixture with at least one of the basic constituents aluminium and magnesium, and that such addition metal should be present in an amount approximating the amount required to form a eutectic mix- 20 ture, we intend to cover slight variations. We have found that if the addition metal is present in amounts within -30 to +30 of the eutectic amount satisfactory results can be obtained.

Any metals which do not meet these requirements are to be excluded, and insofar as this invention is concerned such other metals should be regarded as impurities.

While there are several metals which meet the and which can be used in accordance with the invention, we prefer zirconium as the addition metal: but other addition metal or metals may be added, the latter being taken, for instance, among the following: antimony, chromium, cobalt, beryllium, manganese, titanium, cadmium, nickel, boron, bismuth, molybdenum.

Insofar as zirconium is concerned, this should be added in amounts ranging from 0.05 to 0.2%, preferably 0.18%, to obtain the best results, although amounts up to 2% may be used with the desired results. The lower and upper limits for zirconium are respectively 0.01% and 3%.

As specific examples of the invention, a satisfactory alloy can be made with:

> Magnesium, more than 50%. Zirconium, 0.2%. Aluminium, the remainder.

Are to be considered as preferred alloys the  $_{50}$ following:

> Magnesium, within 85% to 96%. Zirconium, up to 2%, preferably 0.2%. Aluminium, the remainder.

but not necessary, to add them in proportions approximating those corresponding to the eutectic points formed by these addition metals with the base metals. These proportions are well known to those skilled in the art, and as has been indicated, can be obtained from phase diagrams in the technical literature.

For example, the following table is given in which the amounts of the addition metals are the approximate values of the proportion correspond- 65 ing to the eutectic of the binary diagram of aluminium and the addition metals:

	Per cent	
Antimony	1.1	
Chromium	0.40-0.77	
Cobalt		
Beryllium		
Manganese		
Titanium		
Cadmium	. U.13	
Cadmium	. 2	7

As an example, we may have an alloy meeting the requirements of the invention and which consists of:

Magnesium, 85% to 96%.

Zirconium, 0.02% to 2% preferably 0.2%. Titanium, 1%.

Aluminium, the remainder.

A preferred example using titanium is as fol-

Magnesium, 85% to 96%. Zirconium, 0.02% to 2%.

Titanium, 0.2%.

Aluminium, the remainder.

Another example is as follows:

Magnesium, 85% to 96%. Zirconium, 0.08% to 0.11%.

Titanium, 0.08%.

Aluminium, the remainder.

Alloys of the compositions just recited showed very good results when subjected to the action of a corrosive agent.

In all instances the surface of the alloy at the end of the period was covered with protective film. It was found that the protective self-healing film formed more rapidly where the immersion was continuous.

Mechanical properties of the alloy were found to be particularly good when the alloy is rolled. requirements for the addition metal given above 30 A breaking strength of 45 kg. and an elongation of the order 17% were obtained.

> The titanium may be replaced by other metals provided the conditions referred to above are carried out. The following metals, for example, may be used if proportions preferably approximate the eutectic proportions, as indicated below, are observed:

	Per c	ent
	Cr	
40	Be	<2
	Mn	<3
	Co	<2
	Sb	<5
	Ni	<5
45	Cd	<5

Use may also be made of the following as the fourth metal, in proportions preferably less than

> Boron Bismuth Molybdenum

We have found that alloys produced according to the invention may be further improved by As for other addition metals, it is preferable, 55 heat treatment, notably tempering. This heat treatment is designed also to improve the fineness of precipitation of the crystals formed by the addition metals as well as the so called "beta" crystals β (AlaMg2).

The temperature and duration of the heat treatment depend both on the percentage of additions and the magnesium content of the alloy.

The tempering is not carried to as great a degree when the alloy has a high magnesium content, but, in each case, the duration and temperature thereof have an optimum value. It is particularly important that the duration and temperature should not be carried to coalescence of the precipitated granules.

In the case of an alloy to be rolled, the rolling operation is preferably carried out after annealing at a temperature ranging from 410 to 480° C. and cooling.

The heat treatment for giving resistance to 75 corrosion is then carried out at a temperature ranging from 245 to 320° C., preferably close to this last mentioned value. If it is advisable to effect a supplementary rolling operation, a new treatment is carried out at a temperature of 400° or more. In a general manner, for the alloys with which the invention is concerned the tempering should be used if the ingot or rolled plates have been very rapidly cooled. The desired structure of the alloy may also be obtained directly by

suitable slow cooling of the ingot or of the sheets during the rolling, for example, by stopping for about fifteen minutes starting from a temperature generally above 300° C., in which the granules can precipitate.

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