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ALUMINUM BASE ALLOYS HAVING IMPROVED HIGH TEMPERATURE PROPERTIES AND METHOD FOR THEIR PRODUCTION

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ABSTRACT OF THE DISCLOSURE

An aluminum base alloy composition which has improved high temperature and corrosion resistant properties which contains a base comprising either aluminum or an aluminum alloy which has uniformly dispersed therein a nitride of a metal selected from the group consisting of metals belonging to Groups II-A, III-A, V-A and VI-A of the Periodic Table of Elements.

This application is a continuation-in-part of copending United States patent application, Ser. No. 401,999, which was filed Oct. 6, 1964, which is now abandoned.

The instant invention relates to an aluminum base alloy which has improved high temperature properties, which alloy contains a metal nitride or a combination of a metal nitride and a metal, and a method for the preparation of such an aluminum base alloy.

In recent years, aluminum has been found to have wide application in heat resistant construction materials, which materials are required to have high temperature strength and creep strength. For example, aluminum has been employed in internal combustion engine parts which are utilized so as to lighten the vehicles and vessels into which they are incorporated. Furthermore, aluminum has been employed in cast processing materials which are incorporated in the fuselages of jet planes and in conductor materials such as power transmission wires. In light of the numerous uses which have been found for aluminum alloys there has been an increased demand for such alloys which have good heat resistance which would make them suitable for uses under conditions in which the temperature inevitably rises. An example of this is in the field of conductor materials where, due to increasingly larger loads of electrical current which are demanded, there is a substantial rise in the temperature of the conducting material. If said material does not have excellent heat resistant properties, it will soften at these increased operating temperatures. For this reason, in the past, aluminum has not been employed as a conductor material where such a material would be subjected to temperatures exceeding approximately 90° C. and therefore aluminum alloys with high heat resistance have been greatly sought after.

In general, aluminum of industrial purity has a recrystallization temperature in the neighborhood of between 150° C. and 350° C., and furthermore, such aluminum has a very low resistance to heat and exhibits a softening phenomenon at a temperature in the range of between 100° C. and 200° C. Therefore, aluminum alloys have been developed; however, these alloys have not attained a sufficient degree of heat resistance. Usually, upon heating for several hours to a temperature of between about 150° C. and 200° C., they demonstrate a strength loss to such an extent that their strength after heating is

only about 60-80% of the strength of said alloys prior to heating.

In addition to high heat resistance, it is also desirable that aluminum base alloys be resistant to corrosion. There have been many alloys prepared in the past such as those which contain tin as one of the necessary alloying ingredients, which alloys are not suitable as base materials for the instant invention. Inasmuch as said alloys are not corrosion resistant nor do they have the necessary degree of heat resistance, such alloys which contain tin are conventionally employed when it is desired to have an aluminum base alloy with certain improved galvanic properties.

Therefore, it is an object of the instant invention to provide heat resistant aluminum base alloys which have improved high temperature and corrosion resistant properties.

Another object of the instant invention is to provide aluminum base alloys which are useful in numerous construction materials, which construction materials are required to be employed under conditions such that a rise of temperature is inherent in the use thereof.

Yet another object of the instant invention is to provide a method for preparing heat resistant and corrosion resistant aluminum base alloys.

These and other objects of the instant invention will become more evident from the following more detailed description thereof.

We have found that if one disperses a metal nitride or a combination of a metal nitride and a small quantity of a metal homogeneously in a base, one obtains an alloy which has highly improved heat resistant properties and other excellent high temperature properties. Furthermore, we have also found that the high temperature resistant aluminum alloys of the instant invention can be economically produced without the necessity of complicated and expensive production procedures by the above-noted addition of the nitride or mixture of a metal nitride and a metal to a base of aluminum.

In general, we have found that if one uniformly disperses into a base comprising either aluminum or aluminum alloy from about 0.001 to about 2% by weight of at least one metal nitride selected from the group consisting of Group II-A, Group III-A, Group V-A and Group VI-A of the Periodic Table of Elements, one obtains a high heat resistant aluminum alloy. Preferably, the metal nitride is a nitride of a metal selected from the group consisting of Be, Mg, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo and W. In addition, we have found that one may also employ in lieu of the metal nitride a combination of such a nitride with one of the above-noted metals in a combined amount which does not exceed approximately 2% by weight.

By the term "aluminum" as used in the instant specification and appended claims applicants intend to define a pure aluminum or an aluminum of industrial purity which contains between 98% and 99.8% aluminum. Such an industrial purity aluminum may also contain impurities such as silicon, iron, copper and titanium and may be prepared by ordinary, conventional industrial methods. The term "aluminum alloy" is intended to define a heat resistant aluminum alloy which is conventionally employed for casting, which alloy is known alternatively as Y alloy, Lo-ex alloy or hypereutectic aluminum-silicon alloy, an aluminum alloy which is suitable for use in conductors such as Aldrey or Alzur. All of these high heat resistant aluminum alloys contain as the alloy component at least one metal of silicon, copper, magnesium, iron, nickel, zirconium and beryllium. These particular alloy components are employed inasmuch as they result in an aluminum alloy which is highly heat resistant and non-corrosive. Other aluminum alloys which contain dif-

ferent alloy components which do not have high heat resistance and corrosion resistance are not suitably employed as base alloys and therefore not included within the above definition of aluminum alloy. That is to say, that those aluminum alloys which do possess high heat resistance, which alloys are prepared by the incorporation of the above delineated alloy components or equivalent alloy components, are the only ones which are suitably employed as base alloys. Other aluminum alloys such as, for example, those containing tin, which alloys are not corrosion resistant but rather highly corrosive, are not suitable for use as base alloys in connection with the instant invention.

The metals which are employed to form the metal nitrides of the instant invention or which are added in addition to the metal nitride of the instant invention are members of Groups II-A, III-A, V-A and VI-A of the Periodic Table of Elements. These metal nitrides can readily be prepared by contacting said metals with nitrogen at high temperatures. The metal nitrides include those metal nitrides which have a free energy of formation greater than or equal to that of aluminum nitride as, for example, nitrides of the metals contained in Group IV-A (which are for convenience referred to as metal nitrides in Class 1). In addition, the useful metal nitrides include those which have a free energy of formation smaller than that of aluminum nitride as, for example, those contained in Group II-A, V-A and VI-A (for convenience these are referred to as metal nitrides in Class 2). Also included within the term "metal nitrides" are the numerous forms of nitride which some of the metals may form such as Cr_2N , CrN , etc. All of the forms of the metal nitrides may be employed in connection with the instant invention. However, as a matter of course, it is best to add the most stable nitride formed.

In theory, when a nitride of Class 1 as denoted above is added to molten aluminum, it is finely distributed in said molten aluminum without undergoing further reduction by said aluminum and, at the time of casting, this composition acts as a nucleus and contributes to the fineness of the casting structure. It is this composition which results in an improvement in the strength and heat resistance of the material in the form of dispersion hardening by fine particles, precipitating in, or on the boundary, of micro grains. These effects are far superior to those attained by the mere addition of metal elements to conventional alloys. When the thus obtained composition is rolled and then heat treated, or when it is made into electrically conductive materials such as wires and subjected to elevated temperatures such as, for example, by a large load of current, said dispersed particles impede the progress of the recrystallization of aluminum, thus enhancing its heat resistance.

When a metal nitride in Class 2 is added to a molten aluminum, part of this nitride is reduced by said molten aluminum (at a rate of 10% per hour). Therefore, there exists in the molten aluminum, metal and nitrogen formed by said partial reduction, together with the residual nitride, at the time of casting the residual nitride gives rise to the hardening and the effect of fineness which results because of its action as a nucleus. Simultaneously, the metal and nitrogen formed by partial reduction serve so as to strengthen the matrix and result in improved heat resistance.

Furthermore, these nitrides are soluble in the solid state in aluminum. In this case, the atom-like nitrogen is absorbed in vacancies related to dislocation within the aluminum to give stabilization of elastic strain field. In other words, it brings about improvement in the strength and heat resistance by the so-called Cottrell effect.

The conjoint use of more than one nitride having the same crystal structure can result in an even greater effect upon the increase of the strength of a composition as compared with the use of only one nitride. It is considered to be a composite effect brought about by the formation of a double nitride by mutual dissolution of said nitrides. As

examples of these conjoint uses, there are those of face centered crystal nitrides of metals in Group IVa and Va and those of hexagonal closed crystal nitrides of the metals of Group VIa.

When a nitride is added to a molten heat-resistant aluminum alloy containing such metals as Cu, Ni, Si and Mg as alloy component, for instance, such alloys as Y alloy, Lo-ex alloy and hypereutectic aluminum-silicon alloy, its heat resistance is further improved in the form of dispersion hardening by fine particles and at the same time its strength is increased by mutual interference of these nitrides and alloy component. When this material is T5 treated (the tempering treatment of the casting with the quenching treatment omitted) or T6 treated (the quenching, and subsequent tempering, treatment of the casting) in accordance with ASTM, an alloy component such as Si, Cu, Mg and Ni is precipitated. At this time, the precipitate includes the added nitride, thus bringing about the improvement of strength and heat resistance. The same explanation holds when both of the nitride and the metal are added in accordance with this invention.

It will be understood from the foregoing explanation that nitrides which are not homogeneously mixed with aluminum (for instance, Si_3N_4) or a very decomposable nitride (for instance, Cu_3N_2) are not suitable for application in connection with the instant invention. The foregoing theoretical discussions are not intended to in any way restrict this invention, but are believed to be pertinent and fully substantiated by the results of microscopic observation or by tests in strength and high temperature properties which have been carried out using the product in accordance with this invention.

The amount of nitride to be incorporated in the composition in accordance with this invention is about 0.01 to about 2.0% by weight against aluminum, and when both of said nitride and metal are added, a combined amount should not exceed about 2.0% against aluminum.

An amount below the said lower limit is not sufficient to give rise to the desired heat-resistance and strength. On the other hand, when the amount of nitride or nitride and metal combination exceeds the upper limit, unfavorable effects are exerted upon the castability, moldability and electric conductivity. Particularly preferable amount of content is, though varying with the types of the applied nitrides or metals or the use of the products, roughly 1 to 2% for the improvement of heat resistance of thermally resistant construction materials and less than 1% for the obviation of the decrease of electric conductivity in conductor materials. Thus, in accordance with this invention, there can be presented aluminum alloys having markedly improved resistance to heat, mechanical properties and electric conductivity and corrosion resistance as compared with ordinary aluminum or those alloys which contain as the alloy component metals other than the known thermally resistant alloys, Si, Cu, Mg, Fe, Ni, Zr and Be or their equivalents which will result in alloys which are high temperature resistant and corrosion resistant. These properties can be easily judged from a test in tensile strength, creep strength at high temperatures or measurement of electric conductivity of the alloys.

A method of producing an alloy composition of this invention comprises mixing at least one nitride of the metal selected from the group consisting of Be, Mg, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo and W with a molten aluminum or aluminum alloy in the absence of an oxidizing gas at a temperature below the melting point of the said nitride to form a mother alloy in which said metal nitride or metal is dispersed in the aluminum, melting the obtained mother alloy with the addition thereto of said nitride in the amount of about 0.01 to about 2.0% by weight based on the weight of aluminum or aluminum alloy or of said metal nitride and said metal in a combined amount not exceeding about 2% by weight to form a uniformly dispersed phase, and thereafter solidifying it by cooling.

The said mother alloy may include both a metal nitride and an added metal at the same time.

The method of the manufacture of the said mother alloy is further explained.

As a result of experiments, we have found that any attempt to dissolve a metal nitride directly in aluminum in the presence of an oxidizing gas such as air resulted in a failure to disperse said nitride homogeneously. When a metal nitride is added to a molten aluminum in air, both remain separated from each other and never closely dissolved in each other. Even if both are mixed with each other and heated in the form of fine powder, the result is the same. Much to our surprise, however, the above-mentioned problem of failure has been completely solved by practicing the foregoing procedure in the absence of an oxidizing gas, for instance under vacuum and preferably in the presence of an inert gas such as nitrogen or argon. Such being the case, it is presumed that the non-formation of a uniform dispersion phase by aluminum and nitride under an oxidizing atmosphere is mainly ascribable to the fact that the surface of the nitride is oxidized and thus covered with an oxidized coating. In accordance with the method of this invention, it is possible not only to form a uniformly dispersed phase easily, but also to prevent the loss of nitride caused by oxidation.

Furthermore, according to the above-mentioned method which is practiced in the absence of an oxidizing gas, it is possible to adjust the operational temperature to below the melting point of the used metal nitride. To put it another way, it is easy to disperse a metal nitride in an amount up to around 30% by weight uniformly in an aluminum base within a time as short as about 30 to 60 minutes at a relatively low temperature such as 800° C. Heretofore, a method of dissolving a metal nitride in aluminum as an alloying element has been completely unknown. The probable reason for this is that it has never been anticipated that a metal nitride having a melting point as high as 1800 to 3000° C., can be dispersed and dissolved in aluminum in a simple manner, and that any attempt at such method, if made at all, was unsuccessful. It is well known in the art that the dissolution in aluminum or other metal elements or compounds having high melting points ought to be carried out at very high temperatures by using a complicated method or requiring a prolonged time, and that the amount which can be dissolved is small, usually less than 5% and 10% at the most, to say nothing of the fact that there has hitherto been practiced no method of dissolving a metal nitride uniformly in aluminum as an alloying element.

In the preparation of a mother alloy, the shape of the metal nitride is not particularly limited, but in order to increase the speed at which it is dispersed in aluminum, it is preferable that the nitride should be used in the form of finely divided particles usually in the form of particles ground to the fineness of 6 to 8 mesh or less. At this time it is not necessary for the nitride to be melted itself. It forms a compound of a solid phase with a molten aluminum by the action of diffusion. When an oatmeal-like mixture of this finely divided compound with molten aluminum are solidified by cooling, the desired aluminum base alloy is obtained. Namely, the method of this invention is based on a melting process within the range of the temperature at which a solid base and a liquid phase are co-existent if shown in an equilibrium diagram. This is the reason why the method of this invention is practicable even if the heating temperature is, for instance, 800° C., which is far lower than the melting point of the nitride.

In accordance with this method, it is possible to easily produce an alloy containing a nitride in a concentration as high as up to about 30% in a short time. Therefore, the amount of a metal nitride is determined depending upon the desired concentration in the alloy. In general, a mother alloy to be used preferably has a nitride in a concentration of about 5 to 20%.

The foregoing detailed explanation of a mother alloy containing a nitride is also applicable to the manufacture of a metal-containing mother alloy to be used in the production of the aluminum alloy of this invention which contains a metal together with a nitride.

It is preferable that a metal nitride-containing mother alloy and a metal-containing mother alloy should contain only one kind of metal nitride or metal, respectively. This is because, in the manufacture of the aluminum base alloy of this invention, a desired type and amount of a nitride or a metal to be added can optionally be adjusted by choosing the type and amount of said mother alloys. However, it is also possible to prepare and thus use a mother alloy containing a plurality of nitrides, a mother alloy containing a plurality of metals or a mother alloy containing a combination of nitride and metal.

When the thus obtained alloy is added to, and thus dissolved, in a great quantity of molten aluminum or aluminum alloy base in a specified amount to form a uniform dispersion phase and thereafter cast or processed by other ways into shapes of convenience, there is obtained a heat resistant aluminum base alloy which is a desired final product. When a mother alloy is dissolved in a base aluminum, the absence of an oxidizing gas is no longer necessary; it is possible to operate in air. Of course, it is possible to prepare a final product by adding a nitride directly to a great quantity of molten aluminum base without preparing a mother alloy from it. This is, however, an uneconomical and industrially impracticable method to treat such a great quantity of matter, since the operation ought to be performed in the absence of an oxidizing gas as in the above-mentioned manufacture of a mother alloy.

The alloys of this invention which can be obtained in accordance with the procedures detailed above have high recrystallization temperature and elevated strength at high temperatures, which make them fit for use as processing materials for structures which are accompanied by the rise of temperature during use.

Furthermore, the alloys of this invention, particularly those for processing, have in general more excellent corrosion resistance to an aqueous solution than the previously known aluminum alloys. Various aluminum alloys have been proposed up to date in an attempt at the improvement of heat resistance and strength of aluminum, but they have generally far lower corrosion resistance to an aqueous solution than aluminum itself. Though this is a sacrifice unavoidably attendant on an aluminum alloy, it is of course desirable that it does not get too large. In the alloys of this invention, said sacrifice is generally very small. Particularly, an aluminum base alloy containing zirconium nitride exhibits corrosion resistance slightly lower than high purity aluminum.

The alloys of this invention have generally high hardness, and in particular casting alloys exhibit excellent wearing resistance. Excellent hardness is attained especially in the alloys containing a nitride of titanium, zirconium, vanadium, tungsten or tantalum. Those alloys containing a nitride of titanium, vanadium, tungsten or tantalum also have excellent resistance to wearing.

When the alloys of this invention are used as conductor materials, it is desirable to choose those containing a nitride of Zr, Ti, Hf, Be, Ta, Nb or Mg. Particularly preferable is one containing zirconium nitride. It is recommended at the same time that they should not contain Ti, V, Cr, Mo or W alone, because, owing to low electric conductivity of these metals, the electric conductivity of said materials may somewhat be lowered. Hence, in the manufacture of alloys for use as conductor materials, care ought to be taken to avoid the use of a nitride of V, Cr, Mo or W (nitride to be partially reduced by molten aluminum) or the conjoint use of TiN and metallic zirconium capable of reducing it, and thus to use other nitride or a combination of this with metal.

The manufacture of a mother alloy, or an aluminum base alloy in which to use a mother alloy, and various

properties of the thus obtained alloys will be illustrated by the following examples. However, this invention is in no way limited to them.

was polished. A microscopic observation of the section revealed that each of the nitrides was homogeneously dispersed in aluminum.

TABLE I

Metal nitride used	Furnace used	Amount of metal nitride added (wt. percent)	Temperature (° C.)	Net time for heating at specified temperature (hr.)	Stirring with or without
Example:					
1.....	Be ₃ N ₂ A	10	800	1.0	Without.
2.....	Mg ₃ N ₂ A	10	800	1.0	Do.
3.....	TiN..... A	10	1,100	1.0	With.
4.....	ZrN..... B	20	800	0.5	Without.
5.....	HfN..... B	5	1,100	1.0	With.
6.....	VN..... B	10	1,200	1.0	Without.
7.....	NbN..... A	5	1,100	0.5	Do.
8.....	TaN..... A	10	1,050	1.5	With.
9.....	Cr ₂ N..... A	30	900	0.5	Without.
10.....	Mo ₂ N..... B	10	800	1.0	With.
11.....	W ₂ N..... B	20	1,000	1.5	Do.
12.....	ZrN plus TiN..... A	20	1,000	1.5	Without.
13.....	Zr plus TaN..... A	20	1,000	1.5	With.

EXAMPLES 1-13

Manufacture of mother alloy

Various metal nitrides were dissolved in aluminum in the manner mentioned in Table I. A graphite of alumina crucible was used. Heating was carried out either in an electric melting furnace with siliconit heating elements (A) or in a high frequency furnace (B). These furnaces were such that heating may be effected in vacuum or in an atmosphere of inert gas, and that the addition of a nitride, stirring and the casting of the product may be possible therein while maintaining air-tightness. The crucible was charged with about 200 g. of weighed aluminum, deprived of air and thereafter filled with argon gas. The aluminum was then melted while passing a small quantity of argon gas, followed by adding thereof of various metal nitrides ground to a size of 6 to 8 mesh in a desired proportion by weight to the aluminum. The mixture was maintained at a specified temperature for a specified time. During this melting step, if occasion demanded, the molten substance was stirred for some time by a graphite rod to make the dispersion of the nitride easy. This stirring was done

EXAMPLES 14-21

Production of aluminum base alloy and its properties (I)

These examples relate to heat resistant aluminum base alloys prepared by homogeneously dispersing a metal nitride or a combination of this with a metal in aluminum of industrial purity (99.7% Al, 0.06% Si, 0.15% Fe).

About 200 g., of weighed aluminum of industrial purity were put in a graphite crucible and melted, followed by the addition of one or a plurality of mother alloys obtained in accordance with the foregoing examples in a specified amount. The mixtures were then heated for 1 hour at a temperature of about 800° C., in air to give aluminum base compositions having uniformly dispersed therein various components, as shown in Table II.

Each of these composition samples was rolled into a sheet with a thickness of 1 m./m. Using this rolled sheet, tensile test was carried out at temperatures of 150° C., 250° C., and 400° C. Results are shown in Table II. For the sake of comparison, the same test was performed using aluminum of industrial purity and an alloy comprising said aluminum and 0.5% of metallic zirconium. Results are also shown in Table II.

TABLE II

Example	Base Al	Component added and its content	Results of tensile test at specified temperatures, tensile strength (kg./mm. ²)			
			Room temperature	150° C.	250° C.	400° C.
Control.....	Al of industrial purity.	-----	16.1	12.3	7.1	2.1
14.....	do.....	Plus 0.5% Zr.....	19.3	14.2	9.1	4.8
15.....	do.....	Plus 0.5% ZrN.....	19.6	17.3	13.1	7.2
16.....	do.....	Plus 0.5% ZrN plus 0.2% TiN.....	20.4	18.4	14.2	7.3
17.....	do.....	Plus 0.5% ZrN plus 0.2% Zr.....	20.2	18.2	14.5	8.6
18.....	do.....	Plus 0.3% TiN plus 0.2% HfN.....	20.0	17.7	14.3	7.3
19.....	do.....	Plus 0.3% Be ₃ N ₂ plus 0.2% Mg ₃ N ₂	19.5	17.2	14.1	6.9
20.....	do.....	Plus 0.3% VN plus 0.3% TaN.....	20.4	18.2	14.3	7.1
21.....	do.....	Plus 0.2% W ₂ N plus 1.2% Cr ₂ N plus 0.2% Mo ₂ N.....	21.3	19.4	16.2	7.8
21.....	do.....	Plus 0.2% NbN plus 1.5% Cr ₂ N plus 0.3% V.....	22.1	20.3	17.1	8.3

for the purpose of avoiding a tendency for a nitride of W or Hf having a big atomic weight to segregate gravimetrically. It was observed from a peep window of the furnace that the dissolution of the nitride was pretty quickly effected. After a specified time for heating passed, the molten composition was poured into a casting mold of iron with a size of 5 x 5 x 10 cm., placed in the furnace and cast. After cooling, the product was taken out. The conditions for each example are shown in Table I.

The section of each of the obtained castings, i.e., the aluminum base mother alloys containing metal nitrides,

It is concluded from the foregoing results that the alloys of this invention have markedly excellent strength at room temperature and especially at high temperatures as compared with aluminum material of industrial purity and a combination of this with a metal, and therefore, they are suitable as materials for heat resistant parts.

EXAMPLES 22-37

Production of aluminum base alloys and their properties (II)

These examples relate to an alloy prepared by adding a metal nitride or a combination of this with a metal

to a heat resistant aluminum alloy such as Lo-ex alloy (12% Si, 1.0% Cu, 1.0% Mg, 1.7% Ni, 0.2% Fe, remainder being Al) and Y alloy (0.3% Si, 4.0% Cu, 1.5% Mg, 1.9% Ni, remainder being Al).

The alloys were produced in the same manner as described in Examples 14-21. Metal mold cast material (F treated), tempered material (T5 treated) and quenched and tempered material (T6 treated) were made from the obtained alloys. Using test pieces, prepared therefrom, whose parallel part had a size of 50 mm. in length and 14 mm. in diameter, tensile strength was measured at room temperature and high temperatures. For the sake of comparison, the same test was carried out using a sample of a heat resistant alloy material and a combination of this with 0.5% metallic zirconium. Results are shown in Table III. As will be noted from the results, alloys which contain TiN do not result in aluminum products which

The obtained alloy in which aluminum for electric conductors is incorporated as base was heat treated at 500° C., hot rolled and cold-drawn (3 m./m ϕ). Thereafter, its electric conductivity and tensile strength were measured. The bended quantity at 1,000 r.p.m. for 80 hours was determined by means of a centrifugal creep tester. This serves to show the degree of bending deviation when a conductor material is used as a power transmission wire loaded for a long time. When Aldrey was used, the casting was homogenization heat treated at 500° C., water quenched and processed into stretched wires (with a diameter of 3 m./m.) which were tempered at 150° C. In the similar manner, electric conductivity, tensile strength and creep were measured. Similar tests were carried out using a sample of aluminum material for electric conductors and a combination of this metallic zirconium. Results are shown in Table IV.

TABLE IV

Example	Base aluminum	Component added and its content	Electric conductivity, percent	Tensile strength, kg./mm. ²	Creep bended quantity, m./m.	
					130° C.	200° C.
(Control)	Al for electric conductors.		62.1	18.1	4.6	5.5
Do.	do.	Plus 0.2% Zr	57.2	19.7	2.5	2.3
38.	do.	Plus 0.01% ZrN	61.9	18.8	4.2	5.0
39.	do.	Plus 0.2% ZrN	58.2	21.5	1.7	2.4
40.	do.	Plus 0.2% ZrN plus 0.1% TiN	58.6	21.4	1.9	2.1
41.	do.	Plus 0.2% ZrN plus 0.1% HfN plus 0.1% Hf	58.7	21.2	1.8	2.0
42.	do.	Plus 0.2% Be ₃ N ₂ plus 0.1% TaN plus 0.1% NbN	58.7	21.5	1.3	1.9
43.	do.	Plus 0.2% Mg ₃ N ₂ plus 0.1% TaN plus 0.1% Mg	58.6	21.3	1.4	1.8
(Control)	Al alloy for electric conductors.		56.5	34.3	3.1	4.6
Do.	do.	Plus 0.2% Zr	55.0	36.2	2.5	2.9
44.	do.	Plus 0.2% ZrN	56.7	37.9	1.7	2.2
45.	do.	Plus 0.2% ZrN plus 0.1% TiN	57.2	37.0	1.3	1.7
46.	do.	Plus 0.2% ZrN plus 0.1% HfN plus 0.1% Zr	57.3	36.7	1.1	1.4
47.	do.	Plus 0.1% NbN plus 0.2% VN	57.8	36.0	1.0	1.3
48.	do.	Plus 0.2% Mg ₃ N ₂ plus 0.1% TaN plus 0.1% Ta	57.5	36.1	0.9	1.2

have high tensile strength subsequent to the varying treatment conditions and especially after T6 treatment.

It is concluded from the foregoing results that the alloys of this invention have markedly excellent electric

TABLE III

Example	Base aluminum	Component added and its content	Results of tensile test at specified temperatures, tensile strength (kg./mm. ²)				
			Room temperature			T6 and then 150° C.	T6 and then 250° C.
			F material	T5 material	T6 material		
(Control)	Lo-ex alloy		19.2	23.9	31.5	26.5	21.3
Do.	do.	Plus 0.5% Zr	20.4	24.3	32.6	26.9	20.0
22.	do.	Plus 0.5% ZrN	20.7	24.7	33.2	27.6	22.5
23.	do.	Plus 0.5% ZrN plus 0.3% TiN	21.2	25.0	23.9	27.9	23.4
24.	do.	Plus 0.2% HfN plus 1.1% ZrN plus 0.2% Cr ₂ N	22.3	25.7	35.0	29.4	24.8
25.	do.	Plus 0.2% Be ₃ N ₂ plus 0.4% VN	21.2	25.0	33.7	28.0	22.5
26.	do.	Plus 0.3% Mg ₃ N ₂ plus 0.3% TaN plus 0.2% Cr ₂ N	21.5	25.7	34.8	28.5	23.7
27.	do.	Plus 0.9% Mo ₃ N plus 0.2% W ₂ N plus 0.2% NbN	22.4	26.1	35.2	29.1	24.2
28.	do.	Plus 0.7% W ₂ N plus 0.3% TaN plus 0.2% V	21.4	24.8	33.7	27.8	20.0
29.	do.	Plus 0.4% Mg ₃ N ₂ plus 1.2% Cr ₂ N plus 0.3% W	22.3	24.9	35.3	29.3	24.5
30.	do.	Plus 0.3% Sn plus 0.5% TiN	21.4	25.3	24.1	27.7	23.5
(Control)	Y alloy		25.3	30.5	38.8	32.2	26.6
Do.	do.	Plus 0.5% Zr	25.8	31.1	39.3	33.4	27.5
31.	do.	Plus 0.5% ZrN	26.3	31.8	39.8	34.1	28.1
32.	do.	Plus 0.5% ZrN plus 0.5% HfN	27.1	33.1	41.2	35.4	29.0
33.	do.	Plus 0.8% TiN plus 0.4% ZrN plus 0.2% Ti	27.3	33.4	41.4	35.6	29.5
34.	do.	Plus 0.2% Be ₃ N ₂ plus 0.4% TaN	25.9	31.5	39.5	34.0	28.4
35.	do.	Plus 0.3% Mg ₃ N ₂ plus 0.2% NbN plus 0.9% TaN	27.4	33.5	41.5	35.8	29.7
36.	do.	Plus 0.4% VN plus 0.8% TiN plus 0.2% W ₂ N	27.6	33.8	42.1	36.3	30.1
37.	do.	Plus 1.3% Mo ₃ N plus 0.3% Cr ₂ N plus 0.2% Ta	28.4	34.3	43.0	37.3	31.6

It is concluded from the foregoing results that each of the alloy compositions of this invention have remarkably improved properties as compared with heat resistant aluminum alloy used as a base.

EXAMPLES 38-48

Production of aluminum base alloys and their properties (III)

These examples relate to a composition prepared by adding a metal nitride or a combination of this with a metal to aluminum for electric conductors (0.16% Fe, 0.06% Si, remainder being Al) and aluminum alloy for electric conductors (0.47% Mg, 0.57% Si, 0.10% Fe, remainder being Al).

The alloys were produced in the same manner as described in Examples 14-21.

EXAMPLES 49-54

Wearing property of aluminum base alloy

Various aluminum base alloys as shown in Tables V and VI were prepared by incorporating titanium nitride (TiN), vanadium nitride (VN), tantalum nitride (TaN) and tungsten nitride (W₂N) in aluminum of industrial purity and Lo-ex alloy both employed as base aluminum. Wearing resistance test was carried out using these samples. For the sake of comparison, the same test was carried out using a base aluminum and a combination of this with metallic zirconium. Results are shown in Tables V and VI. The samples are disc-shaped with a size of 30

m./m ϕ . The test was a wearing test against cast iron by means of an Amsler type wearing testing machine.

Each of these alloys containing nitrides has excellent resistance to wearing.

aluminum. Hardness of each of these alloys is shown in Tables VII and VIII. For the sake of comparison, the measurement of hardness was also made of a base aluminum and an alloy composed of this and metallic zir-

TABLE V

Example	Base Al	Metal nitride and its content	Decrease of weight by wearing at a load of 165 kg. (mg.)		
			1×10 ⁴ , r.p.m.	2×10 ⁴ , r.p.m.	3×10 ⁴ , r.p.m.
49.....	Al of industrial purity.....	Plus 0.5% TiN.....	0.5	10.5	31
50.....	do.....	Plus 0.5% TiN, plus 1.0% VN.....	0.2	6.5	17
51.....	do.....	Plus 1.5% W ₂ N.....	0.1	4.1	11
(Control).....	do.....	do.....	10	46	95
.....	do.....	Plus 0.3% Zr.....	7	33	66

TABLE VI

Example	Base aluminum	Metal nitride and its content	Decrease of weight by wearing at a load of 100 kg. (mg.)		
			1×10 ⁴ , r.p.m.	2×10 ⁴ , r.p.m.	3×10 ⁴ , r.p.m.
52.....	Lo-ex alloy.....	Plus 0.6% TiN.....	1.4	1.9	4.3
53.....	do.....	Plus 0.5% TiN, plus 1.3% VN.....	0.2	0.4	2.1
54.....	do.....	Plus 0.5% TaN, plus 1.4% W ₂ N.....	0.2	0.3	1.7
(Control).....	do.....	do.....	2.2	3.4	7.2
.....	do.....	Plus 0.3% Zr.....	2.0	3.1	6.9

EXAMPLES 55-62

Hardness of aluminum base alloy

Aluminum base alloys as shown in Tables VII and VIII were prepared by incorporating zirconium nitride (ZrN), titanium nitride (TiN), vanadium nitride (VN), tantalum nitride (TaN) and tungsten nitride (W₂N) in aluminum of industrial purity and Lo-ex alloy as base

40 conium. The measurement was made by means of a Micro-Vicker's hardness tester (50 g. of load) using each of the samples prepared from a sheet rolled by 96% reduction which was heated for one hour at specified temperatures and thereafter cooled. The F, T5 and T6 in Table VIII are as hereinabove explained.

45 These nitride-containing alloys have excellent hardness.

TABLE VII

Example	Base aluminum	Metal nitride and its content	Micro-Vicker's hardness (kg./mm. ²)			
			Room temperature	150° C.	250° C.	400° C.
55.....	Aluminum of industrial purity.....	Plus 0.3% ZrN.....	50	49	46	36
56.....	do.....	Plus 0.3% TiN.....	52	52	49	41
57.....	do.....	Plus 0.7% Mo ₂ N.....	74	72	67	52
58.....	do.....	Plus 0.4% VN, Plus 1.4% TiN.....	72	70	64	49
Control.....	do.....	do.....	46	43	38	22
.....	do.....	Plus 0.3% Zr.....	48	48	44	32

TABLE VIII

Example	Base aluminium	Metal nitride and its content	Micro-Vicker's hardness (kg./mm. ²)				
			F	T5	T6	T6 and then 100° C. 1 hr. heating	T6 and then 250° C. 1 hr. heating
59.....	Lo-ex alloy.....	Plus 0.5% ZrN.....	104	116	139	134	122
60.....	do.....	Plus 0.5% TiN.....	106	119	141	137	128
61.....	do.....	Plus 0.5% TiN, Plus 1.3% W ₂ N.....	117	124	155	146	138
62.....	do.....	Plus 1.2% TiN, Plus 0.7% VN.....	119	127	158	150	138
Control.....	do.....	do.....	98	108	130	122	103
.....	do.....	Plus 0.5% Zr.....	102	113	137	128	110

Corrosion resistance of aluminum base alloy to aqueous solution

Aluminum base alloys were prepared by incorporating zirconium nitride (ZrN), titanium nitride (TiN), vanadi-

obtained by adding metal nitrides to the base alloy are far higher than those of the compositions of the present invention. It is clear that the compositions having such a low anti-corrosiveness cannot be practically used as construction materials or conductor materials, and of course they are not included in the present invention.

TABLE IX

Example	Base aluminum	Metal nitride and its content	Decrease of weight by corrosion (wt. percent)			
			After 1 month	After 2 months	After 4 months	After 6 months
63	Aluminum of industrial purity.	Plus 0.5% ZrN	0.23 (0.34)	0.43 (0.31)	0.71 (0.27)	0.81 (0.31)
64	do	Plus 0.5% TiN, plus 0.4% VN	0.29 (0.32)	0.39 (0.32)	0.71 (0.62)	0.89 (0.94)
65	do	Plus 0.2% W ₂ N, plus 1.0% Cr ₂ N	0.31 (0.34)	0.41 (0.39)	0.63 (0.43)	1.08 (0.84)
66	do	Plus 0.10% Sn	0.56 (1.10)	1.04 (2.03)	2.16 (4.11)	2.96 (6.42)
67	do	Plus 0.10% Sn plus 0.50% ZrN	0.75 (1.48)	1.41 (2.33)	2.73 (4.31)	3.74 (6.65)
68	do	Plus 2.0% Sn plus 0.50% TiN	1.07 (2.02)	1.99 (3.37)	3.95 (6.45)	5.25 (9.97)
69	do	Plus 1.0% Zn	0.52 (1.33)	1.21 (2.54)	2.52 (5.11)	3.48 (8.02)
Control	do		0.14 (0.28)	0.26 (0.51)	0.54 (1.03)	0.74 (1.61)
	do	Plus 0.5% Zr	0.19 (0.21)	0.30 (0.46)	0.71 (0.70)	1.02 (0.92)

um nitride (VN), tungsten nitride (W₂N) and chromium nitride (Cr₂N) in aluminum of industrial purity used as base aluminum. Samples with a size of 30 x 40 x 0.5 m./m. were prepared by rolling and dipped in two kinds of an aqueous solution. Thereafter, the decrease of the weight of the sample with the passage of time was measured at room temperature. For the sake of comparison, the same test was carried out using a base aluminum and a combination of this with a metallic zirconium. Results are shown in Table IX. Among the values which indicate the amount of the sample decreased, those described on the upper lines show the results of using as an aqueous solution a saline water in which hydrogen peroxide was added to promote the corrosion (this saline water was prepared by adding 60 g. of NaCl and 3 g. of H₂O₂ to 1 liter of water. During the test, the decrease of H₂O₂ was compensated every one week to adjust the concentration of H₂O₂ to a constant) and those described in the parentheses in the lower lines show the results of using an aqueous solution collected from a river in the industrial district near Tokyo Bay. The result of analysis of this aqueous solution is shown below.

RESULT OF ANALYSIS

pH: 7.4
M alkali degree: 50.5
SO₄²⁻: 1.2 p.p.m.
S²⁻: 0.4 p.p.m.
Cl⁻: 2.2 p.p.m.
Mg²⁺: 3.5 p.p.m.
Ca²⁺: 5.3 p.p.m.

Every measurement test was performed in an open glass vessel. These nitride containing alloys exhibited excellent corrosion resistance almost equal to that of aluminum. In particular, in a corrosion to a river water in the industrial district, a white protecting layer was formed on the surface and thus prevented the corrosion thereafter. It is also of note that those alloys which contained either tin or zinc substantially showed large decreases in weight which clearly indicates that such alloys are not suitable for similar uses as are those of the instant invention.

Therefore, as is clear from Table IX results, the decrease of weight by corrosion of a base alloy consisting of aluminum and tin (or zinc) of those of compositions

We claim:

1. An aluminum base alloy having improved high temperature properties consisting essentially of a base aluminum having uniformly dispersed therein about 0.01% to about 2% by weight of at least one nitride of a metal selected from the group consisting of Be, Mg, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo and W, said base aluminum being selected from the group consisting of aluminum and an aluminum alloy, said aluminum alloy consisting essentially of aluminum and as the alloy component at least one metal selected from Si, Cu, Mg, Fe, Ni, Zr and Be.

2. An aluminum base alloy having improved high temperature properties consisting essentially of a base aluminum having dispersed therein from about 0.01% to about 2% by weight of at least one nitride of a metal selected from the group consisting of Be, Mg, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo and W and at least one metal selected from the group consisting of Be, Mg, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo and W in a combined amount of about 2% by weight, said base aluminum being selected from the group consisting of aluminum and an aluminum alloy, said aluminum alloy consisting essentially of aluminum and as the alloy component at least one metal selected from Si, Cu, Mg, Fe, Ni, Zr and Be.

3. The aluminum base alloy in accordance with claim 1 wherein the nitride is zirconium nitride (ZrN).

4. The aluminum base alloy in accordance with claim 1 wherein the nitride is titanium nitride (TiN).

5. The aluminum base alloy in accordance with claim 1 wherein the nitride is tungsten nitride (W₂N).

6. The aluminum base alloy in accordance with claim 1 wherein the nitride is a double nitride of zirconium nitride (ZrN) and titanium nitride (TiN).

7. The aluminum base alloy in accordance with claim 1 wherein the nitride is a double nitride of vanadium nitride (VN) and niobium nitride (NbN).

8. The aluminum base alloy in accordance with claim 1 wherein the nitride is a double nitride of molybdenum nitride (Mo₂N) and tungsten nitride (W₂N).

9. The aluminum base alloy in accordance with claim 1 wherein titanium nitride (TiN), vanadium nitride (VN) and tungsten nitride (W₂N) are conjointly present.

10. A method of producing an aluminum base mother alloy containing at least one nitride of metal which com-

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prises mixing at least one nitride of the metal selected from the group consisting of Be, Mg, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo and W with a molten base aluminum in the absence of an oxidizing gas at a temperature below the melting point of said nitride whereby said metal nitride is dispersed in high concentration namely, up to 30% by weight in said base aluminum, said base aluminum being selected from the group consisting of aluminum and an aluminum alloy, said aluminum alloy consisting essentially of aluminum and as the alloy component at least one metal selected from Si, Cu, Mg, Fe, Ni, Zr and Be.

11. A method of producing an aluminum base mother alloy containing both at least one nitride of metal and a metal which comprises mixing at least one nitride of the metal selected from the group consisting of Be, Mg, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo and W and at least one of said metals, with a molten base aluminum in the absence of an oxidizing gas at a temperature below the melting point of said nitride whereby said metal nitride and said metal are dispersed in high concentration namely, up to 30% by weight in said base aluminum, said base aluminum being selected from the group consisting of aluminum and an aluminum alloy, said aluminum alloy consisting essentially of aluminum and as the alloy component at least one metal selected from Si, Cu, Mg, Fe, Ni, Zr and Be.

12. A method of producing an aluminum base alloy having improved high temperature properties which comprises mixing at least one nitride of the metal selected from the group consisting of Be, Mg, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo and W with a molten base aluminum in the

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absence of an oxidizing gas at a temperature below the melting point of said metal nitride to form a mother alloy wherein said metal nitride is dispersed in high concentration in said base aluminum, adding the thus obtained mother alloy to a base aluminum in an amount such that said nitride accounts for about 0.01 to about 2.0% by weight of said base aluminum to form a uniform dispersion phase, and thereafter solidifying it by cooling, said base aluminum being selected from the group consisting of aluminum and an aluminum alloy, said aluminum alloy consisting essentially of aluminum and as the alloy component at least one metal selected from Si, Cu, Mg, Fe, Ni, Zr and Be.

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