United States Patent Office

3,355,281

Patented Nov. 28, 1967

3,355,281

METHOD FOR MODIFYING THE PHYSICAL PROPERTIES OF ALUMINUM CASTING ALLOYS

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No Drawing. Filed Apr. 22, 1964, Ser. No. 361,900
5 Claims. (Cl. 75—138)

This invention relates to a method for enhancing the physical properties of metals by the use of additive alloys.

More particularly, the invention pertains to the modification of aluminum casting alloys with an admixture of alkali and alkaline earth metals employed in the form of an aluminum-alkaline earth metal-alkali metal master alloy. Another aspect of the present invention resides in a novel method for preparing the master alloy.

It is known in the art that aluminum-silicon alloys which have been treated with an alkali metal, especially sodium, have grain structures and mechanical properties which are superior to untreated aluminum-silicon alloys. Metallic sodium, for example, has been used commercially to modify the grain structure of aluminum-silicon alloys and to improve the mechanical properties of castings made therefrom. U.S. Patent No. 1,410,461, while describing such a modification method, also recognizes that when metallic sodium is added to the molten casting alloy, the sodium burns resulting in objectionable smoke and fumes as well as the loss of some of the sodium by volatilization. This patent suggests that amount of sodium lost may be reduced by adding the sodium in the form of an alloy with a heavy metal such as zinc. The problems attendant upon the use of metallic sodium are further recognized in U.S. Patent No. 1,657,389, which proposes the use of an alkaline earth metal such as calcium to achieve the desired modification of aluminum casting alloys. However, it has been found difficult to add calcium in trace amounts to the aluminum alloys because of its high melting point and reactivity with both oxygen and nitrogen in the atmosphere. The comparatively high cost of pure calcium can also be detrimental in the commercial use of such a modification method.

One object of the present invention is to provide a novel method for modifying the physical properties of metals or metal alloys such as aluminum-silicon alloys.

Another object of the present invention is to provide a novel method for modifying the processing characteristics as well as the grain structure and mechanical properties of aluminum-silicon alloys which avoids the difficulties and drawbacks of the prior art methods.

A further object of the present invention is to provide an additive alloy comprising aluminum, an alkaline earth metal and an alkali metal which can be employed to modify the physical properties and handling properties of metals such as aluminum-silicon alloys.

A still further object of the present invention is to provide a new and improved method for preparing the additive or master alloy.

These and other objects of the present invention will become readily apparent from the ensuing description and illustrative embodiments.

In accordance with the present invention it has now been found that the physical properties of metals such as aluminum-silicon alloys can be readily improved by the addition thereto of a minor amount of a master alloy of aluminum with an alkaline earth metal and an alkali metal. In general, the master alloy contains about 0.5 to 20% by weight of the alkaline earth metal, about 0.01 to 1.0% by weight of the alkali metal, and from about 79 to 99% by weight of aluminum. The preferred master alloy contains about 4 to 10% by weight of the alkaline earth metal, about 0.1 to 0.5% by weight of the alkali metal, and from about 89.5 to 95.9% by weight of aluminum.

The properties of the master alloy, in the 0.5 to 20% by weight alkaline earth metal range, are such that it can be cast into convenient bars such as round bars having a diameter, for example, of about one and one-half inches. The alloy is also brittle enough to permit simple breaking off of the amounts required in the particular treating operation. Moreover, the alloy is safe to handle, since it does not react with water and contains sufficient treating metals so that the amount needed is easily melted and dissolved by the superheat in the molten metal or alloy.

Only a relatively small quantity of the master alloy additive agent is required to effect the desired changes in the casting metals or alloys. It has been found, for example, that the master alloy need only be added to the aluminum-silicon alloy or other metal composition being treated in amount sufficient to yield from about 0.001 to about 0.10% by weight of the alkaline earth and alkali metals, based on the total weight of the resulting composition. In accordance with the preferred method of operation, the resulting or final metal composition contains only about 0.01 to about 0.05% by weight of total alkaline earth and alkali metals.

Although the alkaline earth metals employed in preparing the master alloys of this invention may be selected from the group consisting of magnesium, calcium, strontium, barium and mixtures thereof; the preferred alkaline earth metal has been found to be calcium. On the other hand, the preferred alkali metal is sodium. It will be understood, however, that other alkali metals such as potassium, lithium, etc., and mixtures of alkali metals may also be employed. For purposes of illustration, the invention will be described more specifically in terms of a master alloy comprising calcium, sodium and aluminum.

As previously indicated the master alloy of this invention can be employed to modify the physical properties of a variety of metals and metal alloys. The invention will be illustrated hereinafter with respect to the use of the master alloy in the modification of aluminum casting alloys containing silicon, magnesium or zinc. Nevertheless, other metals and metal alloys such as, for example, iron and steel may be similarly treated.

The use of the master alloy of this invention to effect metal modification has the further advantages of avoiding the addition of contaminating heavy metals and of not substantially altering the ratio of aluminum to alloying metal in a casting alloy such as aluminum-silicon. In general, aluminum-silicon casting alloys, for example, contain about 3 to 15%, and preferably about 8 to 13% by weight of silicon. Thus, the inclusion of a non-silicon containing alloy in the additive as a vehicle for the alkaline earth and alkali metals does not substantially alter the aluminum-silicon ratio of the final casting metal. More specifically, it has been found that an aluminum-calcium-sodium master alloy carrying a total of 5% calcium and sodium can be added to a 90% aluminum-10% silicon alloy to a level of about 0.01 to 0.05% calcium plus sodium with a resulting change only in the order of one part per hundred in the silicon content. That is, the silicon content would only drop from 10% to 9.9%, which is usually within the variability limits for these constituents in the alloy.

The master alloy of this invention, e.g. a calcium-sodium-aluminum alloy, may be prepared in any convenient manner known in the alloy preparation art. It can be formed, for example, by heating pure aluminum metal in a suitable vessel, e.g. gray cast iron or a graphite crucible, until molten and then rapidly adding calcium and sodium with stirring at about 700° to 1000° C., and preferably at about 750° to 850° C., and holding the temperature in this range until uniform composition is obtained.

It is preferred to carry out this process under an inert gas, for example, in an atmosphere of helium, argon, neon, or a mixture thereof. Another method of preparation of the master alloy involves the electrolysis of calcium and sodium into molten aluminum utilizing a fused salt containing the appropriate $CaCl_2$ —NaCl mixture.

In accordance with another aspect of the present invention, an economical method of preparing the calcium-sodium-aluminum master alloy has been discovered. The starting material is by-product sodium cell filter-sludge having the following typical analysis:

	Percent by weight
Calcium	18–22
Sodium	60–65
CaO, Na_2O, Inerts	13–22

Broadly, however, impure mixtures containing from 9 to 25% calcium, 50 to 75% sodium, and up to 25% inerts may be employed.

In general, the method of preparation comprises agitating a melt containing the aluminum to be alloyed, the sodium-calcium or sodium filter sludge, and molten calcium chloride at a temperature within the range of about 700° to 800° C., preferably under an inert atmosphere. The order in which the ingredients are introduced into the alloying mixture is not critical. For example, all of the components can be charged to the reaction vessel initially. Alternatively, the aluminum may be charged and melted, covered with a layer of calcium chloride, after which the sludge is charged. It is also possible to add the aluminum last to a molten mixture of sludge and calcium chloride.

As the molten mixture is being stirred, calcium and sodium from the sludge dissolve in the aluminum. The amount of calcium which can dissolve, to form a liquid alloy with aluminum, is considerable. On the other hand, sodium is soluble in aluminum only to the extent of about 0.01% by weight. However, an important feature of this invention is the increased solubility of sodium in the aluminum alloy brought about by the presence of calcium in the aluminum alloy. Sodium solubility is increased from a level of about 0.01% by weight to a level of up to about 1.0% by weight. The remaining undissolved sodium in turn reacts to a high degree with the calcium chloride to introduce additional calcium into the calcium-sodium-aluminum alloy in accordance with the following equation:

$$CaCl_2 + 2Na \rightarrow Ca + 2NaCl$$

The resulting admixture of $CaCl_2$ and NaCl acts as a flux to remove the oxides and other inerts which are present in the starting materials. The calcium-sodium-aluminum alloy is separated from the flux by conventional methods such as bottom tapping from a separated two phase (salt-metal mixture) or by solidification and physically separating the metal layer. Either cobbing or solution of the salts in water may be used.

a sludge of known composition and an excess of calcium chloride in relation to the sodium, it can be assumed that substantially all of the calcium in the sludge and about 0.5 wt. percent of the sodium will dissolve in the aluminum and that the rest of the sodium will react with the calcium chloride to produce calcium.

As described above, a method has been developed whereby increased amounts of sodium, derived from a low-cost source (sodium cell filter-sludge), can be introduced into aluminum-calcium master alloys. In addition, sodium from the same low-cost sodium can be used in the same process to generate calcium from calcium chloride. This method contrasts with the use of relatively high cost sodium or calcium when introduced as the pure metals.

The invention will be more fully understood by reference to the following illustrative embodiments.

Example I—Preparation of master alloy

(A) A charge of 40 parts of pure aluminum, 5 parts of metallic sodium and 45 parts of anhydrous calcium chloride was placed in a gray cast iron pot equipped with a steel top tightly fitted and of sufficient height so that the alloy could be poured into the top for cooling into an ingot by tilting the top below the horizontal so that the alloy would flow into the top section. This made for easy removal and separation as the upper salt layer and lower metal layer could be parted easily after cooling. The pot was equipped with a stirrer to effect good contact between sodium, salt and aluminum in the molten state. For melting the pot was placed in a tilting, induction heated furnace with the cool top protruding out of the furnace or heating zone. The closed charged vessel was purged of air with argon prior to heating and maintained under argon blanket for the duration of the run. Temperature was raised to 800° C. and the contents allowed to melt. Then rapid stirring was maintained for 15 minutes. The alloy was allowed to settle for 10 minutes after which the furnace was tilted so that the contents could flow into the cooler upper section. After separation from salt the crude ingot was washed with water, dried, remelted and cast into 1½ inch alloy bars. Results of two separate preparations are set forth in Table I in runs 2 and 4.

(B) In an exactly similar manner a charge consisting of 42 parts of pure aluminum, 10 parts of sodium cell filter sludge (analyzing 20% Ca; 60% Na; 20% oxides and inerts) and 40 parts of anhydrous calcium chloride was put through the heating, agitation and casting cycle. The resulting alloy from several such preparations are shown in Table I, runs 1, 3, and 5. Recovery of metal values in the sludge as calcium plus sodium in the aluminum was 80–96%. The conversion of $CaCl_2$ to NaCl approached 30%.

That aluminum is not functioning as a reducing agent for $CaCl_2$ under these conditions is shown by the fact that no aluminum salts appear in the molten salt layer.

TABLE 1

Run No.	Wt. of Al, lbs.	Wt. of $CaCl_2$, lbs.	Wt. of CaNa, lbs.	Wt. of Pure Na, lbs.	Percent Ca in Bar	Yield on Na, Percent	Yield on $CaCl_2$, Percent
1	4.0	1.0	0.5		8.6	96	72
2	4.0	4.5		0.5	9.1	84	22.5
3	4.2	4.0	1.0		15.3	86	31
4	4.2	3.0		0.5	8.4	81	35
5	2.9	4.7	0.6		4.6	99	21

It is also possible, although less economical, to carry out the aforedescribed process using metallic sodium in place of sodium cell filter sludge as a source of sodium.

The amount of sodium sludge used in proportion to the aluminum in forming the calcium-sodium-aluminum alloy varies with the composition of the sludge and the composiiton desired of the master alloy. In general, using

Example II—Modification of aluminum-silicon alloys

An untreated aluminum-6% silicon alloy was used to produce a block casting. As is typical of this type of casting, the surface of the cast block "pulls" in from the mold surface where the heat is retained for the longest times causing about 5 to 10% of the cast blocks to be rejected.

In commercial practice this effect is avoided to some extent by adding "chilling irons" and extra "risers" to the mold, which undesirably increase the labor expenses both before and after the casting is poured.

In accordance with the present invention this undesirable effect is prevented by the presence of about 0.01 to 0.5% CaNa in the aluminum casting alloy prior to the pouring step. No extra "risers" or "chilling irons" are needed. To effect this treatment, 0.44 lb. of a master alloy comprising 4.5% CaNa in aluminum was placed in a hot ladle followed by the addition of 100 lbs. of molten aluminum-6% silicon alloy. After allowing about two minutes for the usual mixing and skimming operations, the treated casting alloy was poured into sand molds. A refinement in the silicon structure was noted, and a photomicrograph revealed the presence of much smaller silicon crystals. The improvement in tensile strength and hardness properties is shown in Table II.

TABLE II

	Untreated Alloy Casting		CaNa Treated Alloy Casting	
	1	2	3	4
Tensile, p.s.i.	22,600	22,600	23,050	23,400
Percent Elongation	3.0	3.0	4.0	4.5
Rockwell Hardness B Scale	54	50	47	48

Example III—Modification of aluminum-magnesium alloys

To 100 lbs. of an aluminum-6% magnesium casting alloy was added 0.05% by weight of calcium plus sodium in the form of a 4.5% calcium-0.2% sodium-aluminum master alloy. This was accomplished by drawing 100 lbs. of the molten alloy into a ladle, and then adding 1 lb. of the master alloy in one chunk to the surface and submerging it into the molten aluminum by a phosphorizing iron. The master alloy dissolved in less than 1.5 minutes, and the treated aluminum-magnesium alloy was then cast into steel molds. A minimal amount of shrinkage was noted in the casted block after cooling. In contrast, an untreated aluminum-6% magnesium casting alloy gave a cast block product having marked surface shrinkage.

Example IV—Modification of aluminum-zinc alloys

A casting alloy of aluminum-7% zinc was treated in the same manner as described in Example III. Approximately 0.512 lb. of a master alloy comprising 7.8% calcium-0.2% sodium-aluminum was combined with 100 lbs. of the casting alloy to give a concentration of 0.04% by weight calcium plus sodium in the aluminum-zinc alloy. The resulting metal composition was then poured into wheel molds to produce castings which have a thin walled hollow section between the hub and the rim. This thin walled section must hold grease under pressure during service. Castings made with the aluminum-zinc treated as described above showed substantially no porosity and held grease during service. The use of an untreated aluminum-zinc alloy, on the other hand, resulted in castings which were very coarsely porous with a tendency to leak grease. In Table III the improvement in physical properties achieved by treating the aluminum-zinc alloy by the method of this invention is demonstrated.

TABLE III

	Untreated Al-Zn Alloy		Al-Zn Alloy Treated with 0.02% Ca-Na	
	1	2	3	4
Tensile, p.s.i.	29,550	29,950	34,300	34,000
Percent Elongation	2.5	3.0	6.0	6.0
Rockwell Hardness B Scale	44	36	29	30

The above data show that the method of this invention whereby aluminum casting alloys are improved by the addition of master alloys containing a combination of an alkaline earth metal and an alkali metal with aluminum. The improvement in surface phenomena achieved by practicing the present invention is not completely understood. The above data indicate that it may be separate from the refining of the silicon crystal structure, since the effect was also achieved on the surfaces of non-silicon containing aluminum castings. One possible factor may be better contact of the metal or metal alloy with the mold wall resulting in better casting wall-strength by faster cooling. Another possible factor may be the existence of a chemical gettering of gases between the wall of the mold and the hot soft metal. At any rate, the aluminum alloy casting surface is a more accurate replica of the mold surface if the former has been pretreated with a master alloy as described above. Untreated castings are shinier as if they were cast against a gas film, while the treated castings surfaces are a replica of the matte or fine sand finish of the interior of the mold.

Although the present invention has been illustrated by the foregoing specific embodiments, it will be understood that the invention may be subjected to variations and modifications without departing from its broader concepts.

What is claimed is:

1. A method for modifying the physical properties of aluminum casting alloys which comprises adding thereto a property-improving amount of an alkaline earth metal and an alkali metal in the form of a master alloy consisting essentially of about 0.5 to 20% by weight of an alkaline earth metal, about 0.01 to 1% by weight of an alkali metal, and about 79 to 99% by weight of aluminum.

2. The method of claim 1 wherein said casting alloy is an aluminum-silicon alloy.

3. The method of claim 1 wherein said casting alloy is an aluminum-magnesium alloy.

4. The method of claim 1 wherein said casting alloy is an aluminum-zinc alloy.

5. The method of claim 1 wherein said alkaline earth metal is calcium and said alkali metal is sodium.

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