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3,199,979
ALUMINUM BASE CASTING ALLOYS
AND METHOD

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No Drawing. Filed Oct. 27, 1961, Ser. No. 148,051
8 Claims. (Cl. 75-148)

This is a continuation-in-part of application Serial No. 116,929, filed June 14, 1961, now Patent No. 3,128,176 issued April 7, 1964.

This invention relates to improvements in the production of aluminum casting alloys.

In applicant's copending application there are described aluminum alloys and methods which are adapted to overcome many of the problems arising in the use of such aluminum alloys in permanent mold casting and in die casting processes. As discussed therein, one of the difficulties which has heretofore been encountered relates to the high shrinkage that takes place during solidification and cooling. The shrinkage tends to produce voids in the castings as well as shrinkage cracks which render the products unusable. Since the shrinkage defects increase in proportion to the cross-section of the cast articles, they become a considerable factor in the casting of articles of large dimensions. Therefore, excessive losses due to scrap have materially increased the cost of conventional casting processes.

In the field of die casting, problems arise with respect to the inability of the metal to flow during the casting operation whereby the castings will be free from voids, discontinuities, surface roughness and other defects. In addition, the poor flow characteristics will result in the formation of castings of low strength, since the castings are susceptible to failure at the point of such defects. The discontinuities and surface roughness in addition impair the ability to provide a smooth attractive finish, since the defects cannot be easily removed or concealed. It has been found that such discontinuities can result from the presence of a tenacious oxide skin or layer which forms almost instantaneously on the surface of the molten metal. The surface tension characteristics of this oxide film tend to resist wetting out by converging streams of molten metal flowing through the die casting molds. As a result, the surfaces tend to separate and, at times, the fluidity of the molten metal is reduced to a point such that the metal solidifies before the separated areas can be forced together.

Fluidity has been imparted to aluminum casting alloys by the addition of silicon. Thus, aluminum alloys used for die casting have been formulated to contain more than 7% silicon and preferably an amount of silicon between 8.5 to 13%. Aluminum casting alloys with less than 7% silicon have not been considered suitable. Maximum fluidity can be achieved in a formulation containing 10 to 12% silicon; however, at 11.6% silicon the eutectic composition of the metal is reached and the metal will completely solidify almost instantaneously upon cooling. Therefore, the addition of silicon in amounts great enough to impart the desired fluidity tends to aggravate the problem of discontinuity.

Another problem often encountered in the casting of aluminum base alloys is often referred to as "soldering to the die." When this occurs, the cast metal tends to stick to the die and in order to prevent this, iron has been introduced into the alloys in an amount in excess of 1%. A high amount of iron, however, is not desirable, since the iron reacts in the presence of manganese and chromium to form β -iron silicides. The silicides represent hard spots in the casting and they also materially lower the fluidity of the molten metal.

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To overcome these difficulties in accordance with applicant's copending application, aluminum base alloys are provided with calcium introduced as elemental calcium in an amount greater than .002%. The provision of calcium in the manner set forth in the foregoing application has been highly successful insofar as a solution to the above noted problems is concerned. However, it has been discovered that the alloys so produced have suffered from a loss of fluidity when held in a molten state for a period of time. Thus, in a holding period usually not longer than two or three hours, it has been found that the improved characteristics of the casting metal have been lost.

It therefore becomes an object of this invention to provide aluminum base casting alloys which contain calcium in amounts sufficient to improve the properties of the alloys in accordance with the aforementioned copending application and which are also modified to achieve a significant increase in the time during which the beneficial characteristics are retained in the alloys.

It is a further object of this invention to provide an improved method whereby aluminum base casting alloys of the type described in the aforementioned application can be modified to achieve improvements in fluidity and other properties, and whereby the improvements can be retained over long periods.

These and other objects of this invention will appear hereinafter, and it will be understood that the specific examples set forth are provided solely for the purposes of illustration and are not to be considered to limit the instant invention.

One embodiment of the present invention concerns a procedure wherein aluminum base casting alloys containing calcium in amounts in excess of .002% are modified by adding amounts of the rare earth metals in excess of .002% and up to about .02%. Individual rare earth metals may be added to achieve the objects of this invention, or combinations of these metals, with or without other ingredients, can be employed. Thus, cerium additions are suitable for achieving the objects of this invention, and additions of misch metal have likewise proven satisfactory. When misch metal is employed, any of the various commercial forms of the alloy can be utilized. The commercial alloy compositions generally contain a minimum of about 50% cerium along with about 50% lanthanum, neodymium and the other rare earth elements. Typical commercial forms may also lie within the following range of compositions:

	Percent
Ce -----	50-70
Fe -----	1- 5
La, Nd, Pr -----	Remainder

As an additional embodiment of this invention, it has been found that the addition of beryllium in amounts from .002 to .02% of the alloy compositions containing calcium will increase the length of calcium retention in the alloy. Thus, with beryllium additions to the calcium containing alloys, for example, alloys of the type set forth in the illustrations of the aforementioned copending application, the fluidity and other improved characteristics of the castings will last for significantly longer periods.

The described presence of the calcium in the aluminum casting alloys as set forth in the copending application appears to enhance the ability of the aluminum to absorb larger amounts of gases while in the molten state. These absorbed gases are released when the molten metal is converted to the solid state and the gases remain entrapped in the frozen metal to provide voids of pinhole porosity thereby decreasing the density of the cast product and compensating for the shrinkage otherwise tak-

ing place during solidification and cooling. Thus, the presence of calcium apparently operates to avoid the porosity and shrinkage problems heretofore encountered in sand and permanent mold casting. In some cases, it may be preferred to grain refine the alloy to reduce pinhole porosity and thereby to materially increase the strength and other mechanical properties of the castings. The pressure-tightness of the casting can also be thus improved, and the improvements are believed to be due in part to the reduction of shrinkage defects and to the presence of pinhole porosity within castings produced in accordance with this invention.

The introduction of calcium has also been found effectively to modify the characteristics of or eliminate the oxide film formed on the surface of the molten aluminum. The addition of calcium, therefore, produces a condition whereby the converging streams of molten alloy will more readily wet one another for substantially complete and immediate mixture thereof. Therefore, discontinuities heretofore experienced are greatly reduced or completely eliminated.

The presence of calcium in the casting alloys also operates to markedly increase the fluidity of the molten metals. In a die casting operation, it appears that the fluidity is increased noticeably when calcium is employed in the alloys. This greatly enhances the flow of the molten metal in die casting whereby complete filling of the mold can be achieved more rapidly and more effectively.

The marked increase in fluidity which is experienced when the calcium is employed permits a reduction to be made in the amount of silicon in the alloys. Reduction of the silicon to amounts less than 11.6% enables the alloys to depart from a eutectic composition whereby a greater spread between the liquidus and solidus states is obtained. There is, therefore, more time provided in which the metal in a mushy state can be compacted by the pressure of the plunger. Furthermore, it has been found that reduction in the silicon content is desirable since a considerable shrinkage problem has resulted with silicon contents in the neighborhood of 11%, particularly in large castings. Thus, center line shrinkage resulting in actual separation in thick cast members has been discovered in many cases. By dropping to 9% silicon and by modifying the casting alloy in accordance with this invention, the desired fluidity has been obtained without the existence of any shrinkage problem, even in large cast sections.

In accordance with the practice of this invention, the above-noted fluidity and the shrinkage problems are avoided even with alloys containing from 7 to 13% silicon, up to 5% copper and up to .5% magnesium. In addition, alloys containing as little as 3% silicon can now be made for use in die casting operations.

The increase in fluidity which is obtained by the presence of calcium also enables the preparation of alloys with an iron content of less than 1%. Even with the iron reduced below 1%, alloys containing from 0.002 to 0.02% calcium are not susceptible to die soldering. In one case, the iron content was reduced to as low as 0.6% without experiencing die soldering difficulties with 0.01% calcium present in the alloy.

In addition to the above-mentioned improvements, the reduction in iron and silicon made possible by the practice of this invention enables the production of castings with improved shock resistance, impact resistance and tensile elongation.

To illustrate the advantages of this invention, reference is made to tests which were run to indicate the amount of elemental calcium retained over a period of time in molten aluminum base casting alloys. It was found that in alloys such as those set forth in the examples of the copending application, the calcium content would go below the preferable .004% calcium con-

tent and also below the minimum .002% content in a relatively short time. Accordingly, the fluidity and other improved characteristics of the alloys were impaired by reason of the lack of calcium in the alloys.

This condition can be illustrated by the following examples:

Example I

In this example an aluminum base alloy containing 3-4% copper, 9-10% silicon, and maximum amounts of .1% magnesium, 1.0% zinc, 1.2% iron, .35% manganese, .5% nickel and .3% each of other elements was modified by the addition of .01% calcium. The alloy was melted and retained at about 1300° F. Periodic analysis for the calcium content gave the following results:

Elapsed time (hrs.):	Calcium analysis (percent)
Start	.010
.25	.012
.5	.009
.75	.0084
1.0	.0077
1.25	.0071
1.5	.0068
1.75	.0056
2.0	.0052
2.25	.0044
2.5	.0040
2.75	.0032
3.0	.0028
3.25	.0026
3.5	.0022
3.75	.0018
4.0	.0014
4.25	.0014
4.5	.0006
4.75	.0002
5.0	None

As indicated by the results, the calcium content fell below .004% after 2.5 hours and below the .002% minimum after 3.5 hours.

Example II

An aluminum base casting alloy containing 3-4% copper, 5.4-6.5% silicon and maximum amounts of .10% magnesium, 1.0% zinc, 1% iron, 0.6% manganese, 0.25% titanium and 0.3% of other elements was modified by the addition of .015% calcium. The alloy was melted and retained at 1300° F., and periodic analysis for the calcium content revealed the following:

Elapsed time (hrs.)	Calcium analysis (%)
Start	.015
.25	.0125
.5	.0095
.75	.0020
1.0	.0095
1.25	.0080
1.5	.0070
1.75	.0080
2.0	.0060
2.25	.0060
2.5	.0045
2.75	.0040
3.0	.0035
3.25	.0035
3.5	.0030
3.75	.0030
4.0	.0020
4.25	.0030
4.5	.0010
4.75	.0015
5.0	None

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In this instance the calcium content decreased below .004% in 2.75 hours and below the .002% minimum in 4.25 hours.

Example III

An aluminum base casting alloy having a composition similar to that of Example I, but containing .012% calcium along with .004% beryllium, was melted and held at 1300° F. and periodically analyzed for calcium. The analysis was as follows:

Elapsed time (hrs.)	Calcium analysis (%)	
Start	.0121	5
.25	.0127	
.5	.0122	
.75	.0122	
1.0	.0114	10
1.25	.0110	
1.5	.0096	
1.75	.0095	
2.0	.0089	
2.25	.0078	15
2.5	.0079	
2.75	.0074	
3.0	.0067	20
3.25	.0066	
3.5	.0060	25
3.75	.0058	
4.0	.0056	
4.25	.0050	
4.5	.0048	30
4.75	.0043	
5.0	.0039	
5.25	.0038	
5.5	.0032	
5.75	.0028	35
6.0	.0022	
6.25	.0020	
6.5	.0016	
6.75	.0015	40
7.0	.0017	
7.25	.0010	
7.5	.0017	
7.75	.0009	
8.0	.0009	45
8.25	None	

The effect of the beryllium in combination with the calcium is apparent, since the calcium content did not fall below .004% until 4.75 hours had elapsed, and fell below .002% only after 6.5 hours.

Example IV

Even more satisfactory results have been obtained when rare earth metal additives are provided. Thus, where about .020% calcium and .003% misch metal were added to an alloy the same as that of Example II, the following calcium analysis was obtained:

Elapsed time (hrs.)	Calcium content (%)	
Start	.022	50
.5	.021	
1.0	.019	
1.5	.016	55
2.0	.015	
2.5	.014	
3.0	.012	60
3.5	.015	
4.0	.016	
4.5	.020	
5.0	.020	65
5.5	.019	
6.0	.020	
6.5	.020	70
7.0	.018	
7.5	.020	75

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8.0	-----	.016
8.5	-----	.014
9.0	-----	.011
9.5	-----	.011
10.0	-----	.010
10.5	-----	.008
11.0	-----	.007
11.5	-----	.006
12.0	-----	Missing
12.5	-----	Missing
13.0	-----	.006
13.5	-----	.0055
14.0	-----	.0085
14.5	-----	.0044
15.0	-----	.0054
15.5	-----	.0027
16.0	-----	.0034
16.5	-----	.0028
17.0	-----	.0042
17.5	-----	.0010
18.0	-----	.0012
18.5	-----	.0022
19.0	-----	.0034
19.5	-----	.0002
20.0	-----	.0004

In this case, better than .002% calcium was detected after 19 hours. The preferable minimum of .004% calcium was detected as long as 17 hours after initial melting of the alloy. As in the previous examples, the molten alloy was maintained at 1300° F. during the course of the analysis.

Example V

A similar test procedure when carried out on an aluminum base casting alloy containing .008% cerium, .01% calcium, 9.2-10.8% copper, .2-.35% magnesium and maximum amounts of 2% silicon, 0.8% zinc, 1.2% iron, 0.6% manganese, 0.5% nickel and 0.2% of other elements. Alloys of this type, when melted and held for extended periods, have shown the capability of retaining .004% calcium for over 15 hours and .002% calcium for over 17 hours.

Example VI

A test procedure corresponding to the above, when carried out on a casting alloy of the type set forth in Example II and modified with the addition of .017% calcium and .003% misch metal, resulted in the following:

Elapsed time (hrs.)	Calcium content (%)
Start	.017
.5	.0163
1.0	.0162
1.5	.0163
2.0	.0152
2.5	.0152
3.0	.0146
3.5	.0158
4.0	.0134
4.5	.0132
5.0	.0132
5.5	.0126
6.0	.0124
6.5	.0118
7.0	.0110
7.5	.0100

It will be noted that at the termination of the test, after 7.5 hours, .01% calcium remained in the molten alloy. When comparing this with the results of Examples I and II, it will be apparent that a substantially longer holding period is made available for the molten metal by reason of the small misch metal addition.

Example VII

In a test upon an alloy of the type set forth in Example II containing .015% calcium and .01% misch metal, the following results were obtained:

Elapsed time (hrs.)	Calcium content (%)
Start	.0146
.5	.0130
1.0	.0112
1.5	.0112
2.0	.0108
2.5	.0103
3.0	.0099
3.5	.0098
4.0	.0098
4.5	.0098
5.0	.0081
5.5	.0084
6.0	.0087
6.5	.0087

As in the previous example, a large amount of calcium remained in the molten bath after a holding period of 6.5 hours. This example, therefore, further illustrates the ability of the rare earth metal additives to greatly enhance the versatility of calcium modified aluminum base casting alloys.

The above examples illustrate the ability of the additives to extend over a longer period the advantages obtained by the novel calcium modified alloys. Specifically, the fluidity of the alloys of the instant invention is maintained for longer periods and, therefore, greater versatility and efficiency in the casting of the alloys will result. Furthermore, the other advantages above listed which are obtained by calcium modification are not in any way impaired by the additives of this invention. To the contrary, the additives of this invention permit the retention of these improved properties over a much longer period.

Calcium is brought into the aluminum casting alloys with the addition of silicon which has been used to provide fluidity in the aluminum alloy formulation to be supplied to the die casting art. Such calcium finds its presence in the aluminum alloy in the form of calcium silicides, calcium phosphides, calcium nitrides and the like and, when in this form, the calcium is still considered to be a harmful impurity which requires removal to levels below 0.003 and preferably below 0.001%.

Thus, the presence of calcium introduced as elemental metal in accordance with the practice of this invention should not be confused with the presence of calcium in the form of the various silicides, nitrides, phosphides and the like, as previously found in such aluminum casting alloys. The latter are considered impurities and require removal to below a certain low level, while the addition of elemental calcium has been found materially to improve the characteristics of the aluminum casting alloy. In accordance with the practice of this invention, the desired amount of elemental calcium is introduced after the calcium impurities, as heretofore described, are removed to below the maximum for these impurities. Removal of the calcium impurities to below .001% calcium can be effected by chlorination in accordance with well known procedures.

The reduction of calcium phosphides, nitrides, carbides, silicides, etc., to below the minimum value can also be realized when the aluminum-silicon alloys are originally prepared. Thus, it is known to include amounts of silicon along with aluminum oxide during the electrolytic reduction of the oxide, the product of the electrolysis then comprising an aluminum-silicon alloy. If the silicon added to the reduction cell contains high calcium, the calcium materials are eliminated in the reduction cell and an aluminum-silicon alloy, free of calcium, is produced.

The procedure for the introduction of the rare earth

and beryllium additives may vary and the additives can be introduced as solids, in powdered form or in alloys containing high percentages of the elements or combinations thereof. With regard to the additives to the calcium modified casting alloys, it will be understood that the term "misch metal" is not to be considered limiting and other combinations of rare earth metals not specifically designated as misch metal are contemplated. Furthermore, individual rare earth elements in addition to cerium can be employed, and it is also obvious that the rare earth metals can be added along with other non-essential ingredients. Similar reasoning can be applied with respect to the addition of beryllium.

It will be apparent that the improved method and casting alloys disclosed can be modified without departing from the spirit of this invention, particularly as defined in the following claims.

I claim:

1. An aluminum base casting alloy consisting essentially of at least three percent silicon and including calcium introduced as elemental calcium in an amount greater than .002% but less than .02%, at least one of the rare earth metals in an amount greater than .002% but less than .02%, and the balance aluminum.
2. An aluminum base casting alloy consisting essentially of at least three percent silicon and including calcium introduced as elemental calcium in an amount greater than .002% but less than .02%, misch metal in an amount greater than .002% but less than .02%, and the balance aluminum.
3. An aluminum base casting alloy consisting essentially of at least three percent silicon and including calcium introduced as elemental calcium in an amount greater than .002% but less than .02%, cerium in an amount greater than .002% but less than .02%, and the balance aluminum.
4. An aluminum base casting alloy consisting essentially of at least three percent silicon and including calcium introduced as elemental calcium in an amount greater than .002% but less than .02%, beryllium in an amount greater than .002% but less than .02%, and the balance aluminum.
5. The method of preparing an aluminum base die casting alloy containing silicon in an amount of at least three percent, said method comprising the steps of halogenating the molten alloy to remove calcium introduced with the silicon and present in the form of calcium silicide, calcium phosphide and calcium nitride to an amount less than .003%, adding at least one of the rare earth metals in an amount between .002 and .02% and adding elemental calcium in an amount between .002 and .02%.
6. The method of preparing an aluminum base die casting alloy containing silicon in an amount of at least three percent, said method comprising the steps of halogenating the molten alloy to remove calcium introduced with the silicon and present in the form of calcium silicide, calcium phosphide and calcium nitride to an amount less than .003%, adding misch metal in an amount between .002 and .02% and adding elemental calcium in an amount between .002% and .02%.
7. The method of preparing an aluminum base die casting alloy containing silicon in an amount of at least three percent, said method comprising the steps of halogenating the molten alloy to remove calcium introduced with the silicon and present in the form of calcium silicide, calcium phosphide and calcium nitride to an amount less than .003%, adding cerium in an amount between .002 and .02% and adding elemental calcium in an amount between .002 and .02%.
8. The method of preparing an aluminum base die casting alloy containing silicon in an amount of at least three percent, said method comprising the steps of halogenating the molten alloy to remove calcium introduced with the silicon and present in the form of calcium silicide, calcium phosphide and calcium nitride to an amount

less than .003%, adding beryllium in an amount between .002 and .02% and adding elemental calcium in an amount between .002 and .02%.

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