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ENAMELED ALUMINOUS METAL PRODUCT

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This invention relates to vitreous enamel coated aluminous metal products and is more particularly concerned with those products which have as the base portion a heat treatable aluminum magnesium-silicon type of alloy.

Great strides have been made in developing vitreous enamel formulations which are adapted to coating aluminum and aluminum base alloy articles. These formulations can be satisfactorily fired at temperatures below the melting point of aluminum and some aluminum base alloys. While it is necessary to provide an enamel composition which is readily fusible below the melting point of the aluminous metal it is equally important to secure firm adhesion of the enamel to the metal base. Some of the enamel coated products in the past have exhibited areas of poor adhesion with a resultant spalling of the coating during service which, obviously, is highly objectionable.

An intensive investigation has been made to find a heat treatable aluminum base alloy which can be easily worked, possesses a relatively high melting point and provides a base for a spall-free vitreous enamel coating. It has been found that the aluminum-magnesium silicide type of alloy meets the requirements of high melting point, ready workability and strength but has presented problems in maintaining uniform adherence of the enamel under corrosion conditions. Control of the proportions of magnesium and silicon, as well as other elements, is essential, it has been learned. However, such control by itself has not proved to be entirely effective, especially for extruded products and hence there has been a demand for an alloy that will receive and retain an enamel coating under severe conditions of exposure regardless of the manner in which the alloy has been worked. I have discovered that the addition of a small amount of nickel to an aluminum-magnesium silicide type of alloy containing silicon in excess of that combined with the magnesium is highly advantageous to improving adherence of a vitreous enamel coating without detracting from other desirable properties.

It is an object of my invention to provide an enamel coated wrought aluminum base alloy article which possesses a relatively high strength and yet which is substantially free from spalling of the enamel when given conventional pre-enameling surface treatment. Another object is to provide a strong enamel coated solution heat treatable and precipitation hardenable aluminum base alloy article. Still another object is to provide an enamel coated readily extrudable strong aluminum base alloy product which is highly resistant to spalling of the enamel. These and other objects and advantages will be apparent from the following description and examples of the invention.

My invention is predicated upon the discovery that the addition of from 0.1 to 0.4% by weight of nickel to an aluminum-magnesium silicide alloy containing 0.8 to 1.6% by weight of silicon in excess of that required to form magnesium silicide, Mg_2Si, will substantially eliminate the spalling of enamel on an article made of that

alloy and coated with a vitreous enamel where a conventional pre-enameling surface treatment is employed. The alloy also is readily workable, especially by extrusion, and it also responds to solution heat treatment and subsequent precipitation hardening to improve the strength and hardness. The alloy possesses a satisfactory resistance to corrosion thereby prolonging the useful life of the enamel coated article when it is exposed to corrosive conditions. In addition to the foregoing properties and advantages the alloy has a high enough melting point to permit firing of commercial enamel formulations without incipient melting of the metal article.

To obtain the desired properties the alloy must, in addition to nickel, contain magnesium and silicon in proportions sufficient to form from 0.5 to 1.6% by weight of the intermetallic compound, Mg_2Si, and provide at least 0.8%, but not more than 1.6%, silicon in excess of that combined with magnesium. Translated into total magnesium and silicon content, including the required amount of excess silicon, the respective quantities are 0.3 to 1.0% magnesium and 1.0 to 2.2% silicon. These proportions must be observed to gain a high strength and to promote adhesion of the vitreous enamel without melting the alloy during the enamel firing operation. It has been found that adhesion of the enamel is imperfect where only those proportions of magnesium and silicon are used which correspond to those found in the compound Mg_2Si. The employment of 0.8 to 1.6% by weight of silicon above that required to form that compound plus the presence of 0.1 to 0.4% of nickel insures substantial freedom from spalling of the enamel coating in corrosive environments if the alloy article receives the usual pre-enameling surface treatment.

To improve the strength of the alloy while not detracting from other desirable properties, 0.2 to 0.5% copper can be added to the composition.

As mentioned above, the presence of nickel, along with an excess of silicon, is necessary to produce the spall-free condition of the enamel coating. The two elements within narrow limits exert a strong influence upon the bond between the enamel coating and the alloy article. Without them, some spalling is encountered but if present, the article is substantially immune to spalling providing a suitable surface treatment precedes the application of the enamel. In addition to this effect nickel is also beneficial to improving the strength of the enamel coated article, this being an important consideration in many cases. It is especially significant that the increased strength is obtained without sacrificing any loss in adhesion of the enamel coating. To achieve these results nickel should be present in amount of 0.1 to 0.4%. If less than 0.1% is present no significant improvement in resistance to spalling is obtained, while if more than 0.4% is present, there is no further improvement in adherence of the enamel and the resistance to corrosion is adversely affected.

In order to gain the benefits arising from the presence of nickel and the excess silicon, it is necessary to restrict the impurities in the alloy. The iron content, for example, should not exceed 0.25% by weight while the amount of manganese and chromium should not be over 0.03% each. Titanium can be present up to 0.1% but zinc should not exceed 0.05%. With respect to impurities the alloy may therefore be characterized as being of the relatively high purity type.

The alloy can be hot worked by any of the conventional metal working processes and cold worked, if the latter is required, in the same manner as other alloys of the aluminum-magnesium silicide type. In particular the improved alloy can be as readily extruded as the same alloy without nickel and is therefore adapted to the production of moldings and similar products of contoured cross section. It can also be used, of course, for making rolled products, such as sheet.

The desired high level of strength is obtained by heating the alloy article to a temperature above 950° F. but below the temperature at which any of the alloy constituents melt and rapidly cooling it, as by quenching, to a much lower temperature, usually room temperature. Such a treatment causes a solution of soluble elements within the limits of solubility in solid aluminum at the treating temperature. The rapid cooling following the treatment at an elevated temperature preserves to a very high degree the state of solution existing at the high temperature. Although such a thermal treatment may precede the enamel coating and firing operations, or it may follow those operations if the coating can withstand the treating temperature without fusion, it is generally more convenient to combine the enamel firing and solution heat treatments since the temperatures for these treatments overlap or coincide. In any case the exposure to the elevated temperature should be long enough to permit substantially complete solution of the soluble alloy constituents. If the enamel firing and solution treatments are combined, then the enamel coated article should be cooled from the high temperature as quickly as possible without injuring the coating. If the cross section of the article is not too great, cooling in air may be adequate, otherwise an air blast may be required. If the enamel is to be applied in two steps, such as a ground coat and a cover coat, then the rapid cooling need only be effected following the second treatment.

To prepare the alloy article for reception of the enamel coating, the surface should be cleaned and be given any of the well-known pre-enameling chemical surface treatments, such as with the acid deoxidizer type disclosed in U.S. Patent 2,719,796 and the chromate-containing solutions disclosed in U.S. Patent No. 2,544,139, with or without subsequent firing. These treatments are necessary in developing a good bond between the enamel and the metal base.

The vitreous enamels which can be used to coat the alloy article are generally of the low melting point lead borosilicate or lead-free phosphate and silicate types available on the market which can be fired at temperatures between about 850 and 1040° F. These enamels, supplied in dry form, are made into a slurry and applied to the article in any conventional manner such as by spraying, brushing, dipping or stenciling. The article may be completely or only partially coated, depending upon end use of the article. It is to be understood, therefore, that the term coating refers to both conditions. In any case the enamel formulations used should not have a melting point above that of the alloy article. If a ground coat is first applied, the article is fired, then the cover coat is applied and the firing repeated.

It will be appreciated that a variety of colors can be provided by the enamel but coloration can also be produced by treating the metal surface before the enamel is applied and employing a transparent type of enamel coating.

Upon cooling to room temperature some natural precipitation hardening of the alloy will begin and it will gradually progress over a period of months. However, to accelerate the precipitation hardening the coated articles may be heated to a temperature between about 300 and 400° F. for a period of 5 to 24 hours. Hardening in this manner will develop substantially a maximum strength.

The adhesion of an enamel coating is commonly determined by exposure to an accelerated test in a 5% aqueous ammonium chloride solution in accordance with the procedure set forth in the Porcelain Enamel Institute Bulletin A1–1a of June 1956. This test has been correlated with service experience and is considered to be a reliable guide in judging susceptibility to spalling. It is this test which was used in evaluating the samples referred to hereinbelow.

In the following tests alloy A represents my invention while alloy B represents a prior alloy containing no nickel. The composition of the alloys is given in Table I below.

TABLE I

Composition of Alloys

Alloy	Percent Mg	Percent Si	Percent Cu	Percent Ni	Percent Fe	Percent Cr	Percent Ti	Percent Zn
A	0.42	1.30	0.28	0.32	0.15	0.02	0.02	0.00
B	0.85	0.59	0.27	0.00	0.28	0.18	0.07	0.00

The alloys were cast and extruded according to conventional practice in the form of a molding. Sections were cut from the moldings and degreased with a commercial inhibited alkaline cleaner before being sprayed with a commercial enamel in the form of a slurry. An alkaline cleaner was used for this test because it is more sensitive to variations in alloy composition than the acid deoxidizer or chromate types referred to above. The slurry coated sections were fired at 1000° F. for 12 minutes and cooled in air to room temperature. The enamel coating had a thickness of 3 to 5 mils after it was fired. One group of sections was stored at room temperature for two weeks before determining the tensile properties while a second group was precipitation hardened by heating at 320° F. for 18 hours before the tensile test. The results of the tests are given below in Table II.

TABLE II

Tensile Properties of Enamel Coated Extrusions

Alloy	Condition	Tensile Strength, p.s.i	Yield Strength, p.s.i.	Percent Elongation
A	Stored two weeks	31,500	18,300	17.0
B	do	28,500	13,400	18.0
A	Hardened by heating at 320° F.	41,900	36,400	15.5
B	do	39,300	32,300	11.2

The higher strength and satisfactory elongation of alloy A is immediately apparent and demonstrates the improvement gained from the presence of nickel and a substantial excess of silicon over that combined with magnesium. It is also significant that the increase in strength in alloy A was obtained with about one-half the amount of Mg_2Si as present in alloy B.

A portion of the enamel coated sections in the form of 3″ by 4″ panels that had been stored at room temperature for two weeks were subjected to the accelerated Porcelain Enamel Institute test in a 5% ammonium chloride solution at room temperature for 96 hours. The panels were marked off in ½″ squares and the number of spalls noted. Five panels of each alloy were examined and the results averaged. The percentage of squares showing no spalling is referred to as the spalling index.

TABLE III

Spalling Test Results on Extrusions

Alloy:	Spalling index
A	85
B	35

The superior resistance to spalling of the extruded alloy A is evident with respect to alloy B and illustrates the

benefit gained from the presence of nickel and an excess of silicon.

In another series of tests, ingots were cast of alloys having the composition shown in Table IV, alloy C representing my invention and D being an alloy of the prior art.

TABLE IV

Composition of Alloys

Alloy	Percent Mg	Percent Si	Percent Cu	Percent Ni	Percent Fe	Percent Cr	Percent Ti	Percent Zn
C	0.49	1.58	0.29	0.30	0.12	0.01	0.03	0.02
D	0.81	0.58	0.27	0.00	0.43	0.21	0.03	0.10

The ingots were rolled to sheet form 0.064" in thickness by conventional practice. Sections were cut from the sheets, degreased in the inhibited alkaline cleaner, enamel coated and fired by the same procedure as that followed in preparing the extruded specimens except that the firing was done in 10 minutes. One group was tested for tensile properties after standing at room temperature for two weeks and a second group was heated at 320° F. for 18 hours before being tested. The results of the tensile tests are given in Table V.

TABLE V

Tensile Properties of Enamel Coated Sheet

Alloy	Condition	Tensile Strength, p.s.i	Yield Strength, p.s.i.	Percent Elongation
C	Stored two weeks	39,400	24,900	21.2
D	do	28,000	13,300	14.5
C	Hardened by heating at 320° F.	47,200	39,100	12.2
D	do	36,200	28,800	10.0

The higher strength achieved with alloy C is at once apparent and with a substantially lower Mg_2Si content.

The resistance to spalling was determined in the same manner as described above, 3" by 4" panels being exposed to a 5% ammonium chloride solution for a period of 96 hours. The spalling index was found by using the average of five panels. The results are given in Table VI below.

TABLE VI

Spalling Test Results on Sheet

Alloy:	Spalling index
C	50
D	31

The greater resistance to spalling of alloy C as compared to that of D is obvious. It must be remembered that the surface preparation was not one recommended for commercial use but was one employed for test purposes and hence some spalling was anticipated. The surface preparation was designed to reveal relative performance in the accelerated spalling test.

Having thus described my invention and certain embodiments thereof, I claim:

1. A wrought solution heat treated and quenched aluminous metal article having an adherent substantially spall-free vitreous enamel coating thereon, said aluminous metal being composed of an alloy consisting essentially of aluminum, 0.1 to 0.4% by weight of nickel, 0.3 to 1.0% by weight of magnesium and 1.0 to 2.2% by weight of silicon, said magnesium and silicon being present in such proportions as to form 0.5 to 1.6% of the intermetallic compound Mg_2Si with at least 0.8% silicon in excess of that required to combine with the magnesium, and a maximum impurity content of 0.25% iron, 0.03% each of manganese and chromium, 0.05% zinc and 0.1% titanium, said article being characterized by a higher strength and a greater resistance to spalling of the enamel coating than the same article containing no nickel in the alloy base and less than 0.8% silicon in excess of that combined with magnesium.

2. An article according to claim 1 wherein the alloy also contains from 0.2 to 0.5% by weight of copper.

3. An article according to claim 1 wherein the aluminous metal portion of the article thereof is in the form of an extrusion.

4. An article according to claim 1 wherein the aluminous metal portion thereof is in the form of a rolled sheet.

5. A wrought aluminous metal article having an adherent substantially spall-free vitreous enamel coating thereon, said aluminous metal being composed of an alloy consisting essentially of aluminum, 0.1 to 0.4% by weight of nickel, 0.3 to 1.0% by weight of magnesium and 1.0 to 2.2% by weight of silicon, said magnesium and silicon being present in such proportions as to form 0.5 to 1.6% of the intermetallic compound Mg_2Si with at least 0.8% silicon in excess of that required to combine with the magnesium, and a maximum impurity content of 0.25% iron, 0.03% each of manganese and chromium, 0.05% zinc and 0.1% titanium, said article having an internal structure resulting from a solution heat treatment above 950° F. but below the temperature of incipient fusion, quenching and precipitation hardening, said article being characterized by a higher strength and a greater resistance to spalling of the enamel coating than the same article in the same condition containing no nickel and less than 0.8% silicon in excess of that combined with magnesium.

6. An article according to claim 5 wherein the alloy also contains from 0.2 to 0.5% copper.

7. An article according to claim 5 wherein the precipitation hardening results from heating the quenched article to 300 to 400° F. for a period of 5 to 24 hours.

8. An article according to claim 6 wherein the aluminous metal portion thereof is in the form of an extrusion.

9. An article according to claim 6 wherein the aluminous metal portion thereof is in the form of a rolled sheet.

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