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HEAT TREATMENT OF ALUMINUM ALLOYS

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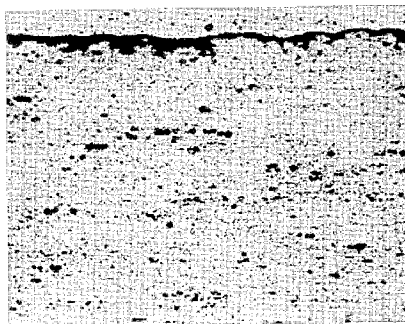


FIG. 1.

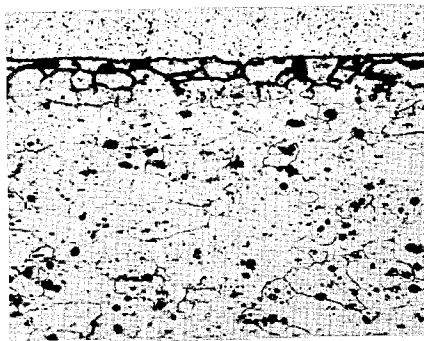


FIG. 2.

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HEAT TREATMENT OF ALUMINUM ALLOYS

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This invention relates to the heat treatment of so-called heat-treatable aluminum alloys, and in particular to a precipitation or aging treatment of such alloys.

The invention further generally relates to a method of improving the adherence of coatings on heat-treatable aluminum alloy surfaces. In particular the invention relates to a precipitation treatment or artificial aging of heat-treatable aluminum alloys which renders the same uniquely responsive to pre-coating chemical etching thereby producing surface characteristics causing firm tenacious adherence of subsequently applied coatings of the type that do not chemically bond with the alloy surface.

The term "heat-treatable" is commonly regarded as including those alloys of aluminum which contain amounts of copper and/or magnesium and/or zinc such that an increase in strength is imparted by suitable thermal treatments, in particular, solution heat-treating and aging. Such alloys also may and usually do contain small amounts of silicon and iron, present as impurities, or positively added as alloying elements, particularly in the case of the former. Furthermore, such alloys may contain very minor amounts of manganese, chromium or nickel. However, these last named elements do not contribute to the response of such alloys to heat treatment, the copper, magnesium and zinc being the critical elements.

Solution heat-treatment entails heating the metal at a predetermined temperature for a period of time sufficient to cause substantially all of the soluble alloying constituents to enter into solid solution followed by rapid cooling, such as quenching in water, to hold most of these alloying constituents temporarily in solution in supersaturated form. In the solution-quenched condition the metal is generally quite ductile but possesses only small or moderate hardness and strength. However, increased mechanical properties, such as tensile strength, yield point and hardness are imparted by aging, which consists of holding the metal at room temperature for a given time after solution heat-treatment (natural aging) or at some elevated temperature (artificial aging or precipitation).

In most instances, the primary objective, dictated by the intended uses of the heat-treatable alloys, is optimum mechanical strength and hardness coupled with as high a resistance to corrosion as is compatible with the attainment of high strength. Consequently, these alloys are normally solution heat-treated and fully aged either

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naturally, that is, at room temperature, or artificially, that is, at elevated temperatures according to established procedures, designed to fully develop strength and hardness. Such alloys are also referred to as high strength or "strong" aluminum alloys.

It has been found, however, that these heat-treatable or strong aluminum alloys when normally solution heat-treated only, that is, heated and quenched from high temperature, or solution-treated and fully aged, do not possess surface characteristics which will cause tenacious adherence of subsequently applied coatings that do not form a chemical bond. In general, a surface which will satisfactorily hold such coatings cannot be obtained by subjecting the metal to an etching treatment prior to application of the coating. The etching solution, for example, an aqueous acid solution, will produce only a pitting of the metal surfaces and subsequently applied coatings are easily peeled off. This condition is observed with many types of coatings, for example, paint, plastics, ceramics and metal plating. In fact, all coatings not chemically bonded to the metal surface are more or less weakly adherent thereto and subject to peeling off.

It is, therefore, a primary object and purpose of this invention to provide heat-treatable or strong aluminum alloys having surface characteristics which upon subjection to pre-coating etching causes subsequently applied non-chemically bonding coatings to firmly and tenaciously adhere to the metal surface.

Another object is to provide a process for artificial aging or precipitation treatment of heat-treatable aluminum alloys to render the metal surface responsive to pre-coating chemical etching in a novel manner whereby the surface will tenaciously and firmly hold subsequently applied coatings, such as metal plating, paint, plastic and ceramic compositions.

A specific object is to provide a process of treating strong aluminum alloys by artificial aging whereby the metal surface when subjected to a pre-coating acid etching is characterized by intergranular fissures which promote a keying action to firmly retain subsequently applied coatings.

A still further object of the present invention is to provide a process for the artificial aging of solution heat-treatable aluminum alloys whereby the alloys are characterized by a condition of optimum susceptibility to intergranular or intercrystalline attack when exposed to corrosive media.

These and other objects and advantages of the invention will be apparent from the following detailed description of the process and products thereof.

It has been discovered according to the invention that the foregoing and other objects and advantages are obtained by thermally treating heat-treatable aluminum alloys to underage the same thereby imparting a condition of optimum susceptibility to intergranular attack when exposed to corrosive media. Such thermal treatment, in general, comprises solution heat treating the alloy, that is, heating under normally prescribed conditions of temperature followed by rapid cooling, and then aging the alloy artificially under correlated conditions of temperature and time sufficient to impart a desirable susceptibility to intergranular corrosion. When the alloy thus thermally treated is subjected to the action of corrosive media, for example, a pre-coating acid etching solution, the corrosive agent selectively attacks the grain boundaries producing deep intergranular fissures and cracks which serve to provide a "keying" action to firmly and tenaciously grip subsequently applied coatings.

The invention makes use of certain principles which recognize that, upon artificially aging solution heat-treated strong aluminum alloys, the soluble constituents, dissolved in the aluminum in the form of a supersaturated solution in the as-quenched state of the alloy, are precipitated and agglomerated first in or near the grain boundaries, and then subsequently within the grains or crystals of aluminum. As the artificial aging temperature is increased above room temperature and/or the time-at-aging temperature is increased, there is an increase in precipitation and agglomeration of these soluble constituent particles. However, in the relatively early stages of artificial aging, this activity is confined to the higher energy levels which are located in narrow areas at the grain boundaries. This precipitation and agglomeration depletes the boundary zones of the constituents in solution and leaves a richer aluminum matrix thus rendering the material more heterogeneous. An electro-chemical potential difference exists between the depleted boundary zones and the grains, and therefore, the grain boundaries, being the higher potential, are selectively attacked in corrosive media to produce the intergranular fissures and cracks.

Normally heat treated strong aluminum alloys, that is, solution heat-treated and quenched, are susceptible to pitting corrosive attack only, since the alloy is more or less homogeneous with the dissolved soluble constituents uniformly distributed throughout the material. So also, with naturally aged heat-treated alloys, since the sub-microscopic precipitated particles are uniformly dispersed.

With normally artificially aged alloys as the time-at-aging temperature is increased, more precipitation and agglomeration occur within the grains and the precipitation once again becomes more or less uniform. At this stage, where the alloy is fully aged (the peak of increase in strength and hardness) or overaged, it is once more susceptible to putting attack only, although not as resistant to intergranular attack as in the as-quenched or naturally aged state, if susceptible to the latter type of aging. Heretofore, in most cases, artificial aging cycles of temperature and time were employed to fully age the alloy, since the more or less uniform precipi-

tation resulting imparted optimum resistance to intergranular attack consistent with the development of maximum strength and hardness in the alloy.

The present invention, therefore, resides primarily in controlling the aging cycle, principally by controlling the time at the selected artificial aging temperature so that precipitation and agglomeration are non-uniform and occur preponderantly in or near the grain boundaries, the aging being halted before precipitation and agglomeration occur markedly within the grains or crystals. However, it is not intended to limit the invention absolutely to the foregoing or any other theory or mechanism of action, it being sufficient to state that the process of controlled artificial aging of the solution heat-treated strong aluminum alloys by curtailment of the time-at-aging temperature produces an optimum susceptibility to intergranular corrosive attack and, therefore, establishes surface characteristics uniquely responsive to etching media, for example, a pre-coating acid etching solution, which, in turn produces a surface which firmly and tenaciously grips a subsequently applied coating.

As indicated above, the solution heat-treatment employed is that normally prescribed for the particular alloy. In general, the alloy is heated to a suitable temperature which is below the temperature at which eutectic melting would occur, and is soaked at such temperature for a time sufficient to dissolve as completely as possible the soluble constituents and to permit homogeneity to be attained by diffusion of the dissolved constituent. Usual temperatures are from about 850 to about 1000° F. depending upon the composition of the alloy. However, the specifications for solution heat-treating these alloys are well-known and do not constitute a part of this invention.

Subsequent to solution heating the alloy is rapidly cooled to room temperature or to a prescribed temperature above that, for example, up to the boiling temperature of water. Various methods of quenching are employed, in particular, a cold water bath, or in some cases a boiling water bath, an oil bath, or even air blasting. It is to be understood, however, that the terms "solution heat-treating" and "solution heat-treated," as defined above, and as used in the appended claims, embrace the step of quenching. Such definition is consistent with the terminology in the art.

In practicing the artificial aging according to the invention the solution heat-treated alloy is reheated at a selected aging temperature of from about 100 to about 500° F. for a predetermined time sufficient to increase the strength and hardness, but leaving the alloy in a definitely under-aged condition thereby developing optimum susceptibility to inter-granular corrosion. In other words, for corresponding temperatures, the aging times employed in the present process are shorter than those required in the normal practice of fully aging the alloy.

Thus, the alloy is artificially aged at the selected temperature under conditions of time such that precipitation and agglomeration of the soluble constituents occurs preponderantly in narrow areas defining the grain boundaries, and heating is discontinued to halt the aging before precipitation and agglomeration can occur markedly within the grains or crystals of the aluminum matrix.

The time at aging temperature may suitably

be selected from the range of from about five minutes to about thirty-six hours. It is, as a rule, essential that the aging times selected from the foregoing range vary inversely with the temperature selected from the range given above. In other words, within the limited ranges given, time and temperature are usually reciprocal. For example, if the aging temperature is only 100° F., the time at aging temperature will be at or in the vicinity of the upper limit of thirty-six hours. Conversely, if the aging temperature is as high as 500° F., the time must be restricted to a few minutes, that is, at or near the lower limit of five minutes. This is generally true with the exception of those alloys which age naturally at significant rates, in which case, the artificial under-aging may be accomplished at the lower temperatures with the time restricted to a few hours.

For proper selection of the aging temperature, the composition of the alloy is an important factor. Certain alloys require higher temperatures before aging is even initiated or at least proceeds at a satisfactory rate, while others are subject to natural aging, that is, at room temperature. However, this invention embraces only artificial aging, even of those alloys susceptible to natural aging, since this latter type of aging imparts high resistance to intergranular corrosion. Artificial aging temperatures have been determined for the known heat-treatable aluminum alloys for the normally prescribed full aging treatment, and, therefore, selection of the proper temperature for the practice of this invention may readily be made for any given alloy.

A preferred temperature range for artificial aging is from about 200 to about 400° F., since substantially all of the heat-treatable alloys may be artificially under-aged within this range with eminently satisfactory results. Moreover, at temperatures as high as 500° F., the time at aging must be extremely closely controlled to avoid fully aging the alloy, if not overaging, and at temperatures as low as 100° F. the aging rate may be so low and the time at aging temperature so extended that the alloy would tend to acquire characteristics similar to one naturally aged, which would tend to result in a lower than optimum susceptibility to intergranular corrosion. Where this narrower temperature range is employed, the time at aging temperature should be from about 1 to about 20 hours.

The artificial aging may be accomplished using any suitable heating means. As examples, there may be mentioned muffle furnaces, or air-circulation furnaces. The manner of cooling the alloy after aging or precipitation treatment is immaterial.

For any given heat-treatable alloy, a number of aging cycles, that is, temperature-time combinations within the ranges set forth above, are available to produce the desired susceptibility to intergranular corrosion with consequent optimum plating and coating characteristics, while simultaneously developing the required strength and hardness. Such suitable aging cycles are empirically determined with particular reference to prescribed conditions or specifications of time and temperature for fully aging the heat-treatable alloy, giving consideration to the type of furnace equipment, size of load, etc.

Several tests, such as the usual corrosion test, using the standard accelerated corrosion medium consisting of 57 grams NaCl plus 10 cc. of H₂O₂ per liter of water; solution potential measure-

ments using an N/10 calomel cell and a solution consisting of 57 g./l. NaCl plus 0.3 g./l. H₂O₂; and microscopic examination of the polished and micro-etched surfaces and internal structures of the alloys subjected to selected aging cycles; were used to determine the plating and coating quality of the heat-treated, artificially aged alloy surface after etching. Of these tests, the latter is the most indicative and reliable. Mechanical properties, such as tensile strength, yield point, elongation and hardness were also determined. Thus, the suitability of any given aging cycle for accomplishing the desired result was confirmed or negated.

The foregoing description of the principles and practice of the invention are applicable to all heat-treatable aluminum alloys, that is, those alloys wherein the copper, and/or magnesium, and/or zinc contents are sufficient to impart the characteristic of precipitation hardening subsequent to solution heat-treatment. In certain notable exceptions, the artificial aging of the invention may be practiced without previous solution heat-treatment, namely, in the case of alloys of aluminum-zinc-magnesium which age without such preceding treatment. Also in cast alloys, as opposed to wrought alloys, those strong alloys which are chill cast are cooled by the mold so as to be supersaturated with respect to the soluble constituents at suitable artificial aging temperatures, and are thus amenable to artificial aging without previous solution heat-treatment.

The invention is further illustrated with reference to the following specific application thereof to the aluminum alloy designated in the industry as 61S, although it is not intended to constitute a limitation of the scope of the invention to such alloy.

61S aluminum alloy consists essentially of from about 0.8-1.2% magnesium, about 0.4 to 0.8 silicon, about 0.35 maximum chromium, about 0.35 maximum copper, and the balance aluminum and the usual minor impurities.

The normally prescribed solution heat-treatment of this alloy, which was employed, consists of heating at about 970° F. for a sufficient time so that all the soluble material is in solid solution at that temperature, and then rapidly cooling by quenching in cold water. In this solution heat-treated condition 61S alloy is designated 61S-T4. In addition, solution temperatures of 940° F., and even 920° F., were employed with somewhat less satisfactory results as compared to 970° F.

The standard or normal artificial aging practices for this alloy consist of soaking or holding the metal, for example, at about 345° F. for six hours, 320° F. for eighteen hours, etc., which treatments result in fully aging the alloy thereby producing the optimum combination of high mechanical properties and good resistance to corrosion. In such solution heat-treated and artificially fully-aged temper 61S alloy is designated 61S-T6. Etching these normally heat-treated (61S-T4) and heat-treated and fully aged (61S-T6) alloys would not produce the desired and critical intergranular fissures and cracks in the alloy surfaces; but rather, the surfaces would merely pit, and uniform adherence of subsequently applied platings or coatings could not be obtained.

In the practice of the invention, applied to 61S alloy, optimum susceptibility toward intergranular attack was obtained by suitable under-aging of the normally solution heat-treated ma-

terial. Among the suitable aging cycles which were employed there may be mentioned heating at 325° F. for 6 hours, 340° F. for 4 hours, and 275° F. for 8 hours. It is to be noted, that for corresponding temperatures, the aging times of these treatments were shorter than those required by the normal aging practices set forth above. Alloy 61S solution heat-treated and artificially aged according to the invention may be herein designated as 61S-T6(x). In practice the preferred aging temperature range for 61S-T6(x) is from about 325 to about 340° F. and the time at aging temperature varying inversely from about 4 to about 6 hours. Satisfactory results have been obtained at these times and temperatures in both laboratory tests and on a production basis with large loads and slow heating-up rates.

The comparative effects of an acid etch on the surfaces of normally heat-treated and aged 61S-T6 and 61S-T6(x) sheet, are at once apparent by reference to the drawings, which are photomicrographs of acid-etched surfaces. Figure 1 illustrates the pitting type of attack, occurring after an acid etch in 10% HCl at 140° F. for 5 minutes on the surface of the normal 61S-T6 sheet. Similar attack was found to occur on 61S-T4 sheet. Figure 2 clearly shows the deep intergranular fissures common to 61S-T6(x) sheet that has been under-aged at 340° F. for 4 hours and acid-etched in 10% HCl at 140° F. for 5 minutes. The internal structures show the effect of the respective aging treatments; Figure 1 with fairly uniform precipitation of small soluble constituents and lack of grain boundary contrast typical of fully aged material, and Figure 2 showing grain boundary outlines and the non-uniform precipitation generally confined to grain boundary areas resulting from the under-aging treatment. It is because of this non-uniform precipitation, almost wholly along grain boundaries, that the unique grain boundary attack is made possible.

One example of the advantages of the invention in the plating or coating art is in the making of selenium rectifiers in the electronics industry. Sheets of 61S-T6(x), prepared by normal solution heat-treatment and artificially under-aged at 340° F. for 4 hours, are first cleaned of dirt and oil in suitable chemical baths, then rinsed, and etched in a 10% solution of hydrochloric acid at an elevated temperature for a period of 1-10 minutes. Then the sheets are rinsed, dipped in 50% nitric acid, and again rinsed in cold water. The sheets are next nickel plated in a Watts bath for 2 minutes at 120° F. This is followed by a cold water rinse and an infra-red drying, after which selenium powder is pressed on at 130° C. at 1500 pounds per square inch for 2 minutes.

The nickel coating is merely a flash coating of approximately .0002" in thickness and does not fill in the intergranular cracks which remained to firmly grip the selenium coating.

The selenium coating does not adhere satisfactorily to either 61S-T4 or 61S-T6 sheet; that is, satisfactory adherence of coatings cannot be obtained unless the metal sheet has been prepared in accordance with the present invention.

The above description is but one example of the uses for heat-treatable aluminum alloys that have been rendered susceptible to intergranular attack according to the invention. Similar uses also include coating with paint, plastics, ceramics

and metals whereby the treated aluminum alloy surfaces firmly grip the coating to provide optimum adherence.

What I claim is:

1. A method of preparing heat treatable aluminum alloy surfaces for reception of non-chemically bonded coatings, comprising the steps of artificially under-aging the normally solution heat treated alloys by heating at a selected temperature within the range of from about 200° to about 400° F. for a predetermined time within the range of from about 1 to about 20 hours, the time varying substantially inversely with the aging temperature, discontinuing said heating when precipitation and agglomeration of the soluble alloy constituents is non-uniform and has occurred predominantly within and adjacent to the grain boundaries, and thereafter subjecting the surface of the under-aged metal to the action of a corrosive media which selectively attacks the grain boundaries producing intergranular fissures which provide a keying action to firmly retain the subsequently applied coating.

2. A method of preparing the surface of heat treatable aluminum alloys for reception of non-chemically bonded coatings thereon in firm and tenacious relation, said alloys containing amounts of soluble constituents selected from the group consisting of copper, magnesium, zinc and mixtures thereof such that increased strength and hardness are imparted by solution heat treatment and aging, comprising the steps of artificially under-aging the normally solution heat treated alloys by heating at a selected temperature within the range of from about 200 to about 400° F. for a predetermined time within the range of from about 1 to about 20 hours, said time varying substantially inversely with the aging temperature, discontinuing said heating when precipitation and agglomeration of the soluble alloy constituents is non-uniform and has occurred predominantly within and adjacent to the grain boundaries, and thereafter subjecting the surface of the metal to the action of an acidic corrosive media to selectively attack the grain boundaries producing intergranular fissures which promote a keying action to firmly retain the subsequently applied coating.

3. A method of preparing the surface of a heat treatable aluminum alloy for the reception of a non-chemically bonded coating thereon, said aluminum alloy containing from about 0.8 to 1.2% magnesium, about 0.4 to 0.8% silicon, about 0.35 maximum copper, about 0.35 maximum chromium, the balance substantially all aluminum and minor impurities, comprising the steps of artificially under-aging the normally solution heat treated alloy by heating to from about 325 to about 340° F. for from about 4 to about 6 hours, said time at aging temperature varying inversely with said temperature, discontinuing said heating when precipitation and agglomeration of the soluble alloy constituents is non-uniform and has occurred predominantly within and adjacent to the grain boundaries thereby imparting to the metal an increased susceptibility to intergranular attack, and thereafter subjecting the surface of the metal to the action of an acidic corrosive media to selectively attack the grain boundaries producing intergranular fissures which promote a keying action to firmly retain the subsequently applied coating.

4. A method according to claim 3 in which the

acidic corrosive media is a 10% solution of hydrochloric acid.

5. A solution heat treated artificially under-aged heat treatable aluminum alloy having an etched surface characterized by firm and tenacious adherence of subsequently applied non-chemically bonded coatings, the said alloy having been artificially under-aged after normal solution heat treatment by heating at temperatures from about 200 to about 400° F. from about 1 to about 20 hours, said time at aging temperature varying inversely with said temperature, said heating being discontinued when precipitation and agglomeration of the soluble alloy constituents is non-uniform and has occurred predominantly within and adjacent the grain boundaries, the alloy in said under-aged condition having increased susceptibility to intergranular attack, and the surface of said alloy having intergranular fissures therein by exposure to the action of a corrosive media which selectively attacks the grain boundaries, said intergranular fissures providing a keying action for firmly retaining the subsequently applied coating.

6. A solution heat treated artificially under-aged aluminum alloy having an acid etched surface characterized by firm and tenacious adherence of subsequently applied non-chemically bonded coating, said aluminum alloy containing from about 0.8 to 1.2% magnesium, about 0.4 to about 0.8% silicon, about 0.35 maximum copper, about 0.35 maximum chromium, the balance sub-

stantially all aluminum and minor impurities, said alloy having been artificially under-aged from the normal solution heat treated condition by heating to from about 325 to about 340° F. for from about 4 to about 6 hours, said time at aging temperature varying inversely with said temperature, said heating being discontinued when precipitation and agglomeration of the soluble alloy constituents is non-uniform and has occurred predominantly within and adjacent to the grain boundaries, said alloy in said under-aged condition having increased susceptibility to intergranular attack, the surface of said alloy being characterized by interangular fissures formed by the action of an acidic corrosive media on said under-aged alloy, said intergranular fissures promoting a keying action to firmly retain the subsequently applied coating.

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