SURFACE HARDENING OF ALUMINUM ALLOYS

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Field of Search 148/6.11, 11.5 A, 20, 13.1, 148/159

ABSTRACT
This invention provides aluminum alloys which have a Vickers surface hardness of about 250 kg/mm² to 1,400 kg/mm². This invention also provides a process for preparing such aluminum alloys by exposing said aluminum to a source of cyanide anion at a temperature of about 450°C to 550°C.

7 Claims, 19 Drawing Figures
SURFACE TREATMENTS OF AL-ALLOYS
TEMPERATURE = 530°C

\[ p = \frac{K}{V} \]

ALLOY-124
ALLOY-244
ALLOY-138

\[ K = 6.23 \text{(average)} \]
\[ K = 6.1 \text{(average)} \]
\[ K = 4.8 \text{(average)} \]

0 12
EXPOSURE TIME (hours)

30 20 10 0
LAYER THICKNESS \( p \) IN 0.001 mm

FIG. 17
SURFACE TREATMENTS OF AL ALLOYS

FIG. 18

- TEMPERATURE = 550°C
- TEMPERATURE = 540°C

ALLOY - 138
ALLOY - 124

LAYER THICKNESS IN 0.001 mm

EXPOSURE TIME (hours)
**TEST CONDITIONS**

- **SLIDING SPEED** = 2.29 cm/seg
- **CONTACT PRESSURE** = 13.6 Kg
- **RING DIAMETER** = 3.5 cm
- **RING WIDTH** = 0.79 cm
- **LUBRICATOR OIL** = SAE 30
- **TEMPERATURE** = 121°C
- **TIME** = 2 HOURS

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**FIG. 19**

- **WEIGHT LOSS (GRAMS)**
  - **MACHINED AND LAPPED**
  - **MACHINED**
  - **AS CAST UNTREATED**
  - **TREATED 4 HOURS AT 540°C**
SURFACE HARDENING OF ALUMINUM ALLOYS

This application is a continuation-in-part of my prior copending application Ser. No. 250126 filed May 4, 1972, now abandoned, and the benefit of the filing date of my prior application is claimed.

BACKGROUND OF THE INVENTION

a. Field of the Invention

It is obvious that the hardening of the surface of aluminum alloys is an extremely desirable phenomenon. Thus, the very best possible use of a lightweight metal such as aluminum could result if the hardness of aluminum could be increased so that it could be utilized in areas where heavier but harder metals (e.g., steel) are now used. To overcome the drawback resulting from the relative softness of aluminum it has been the practice to replace aluminum portions with other metal portions at that point where hardness or surface resistance is critical. Thus, the points of severe wear and abrasion in machine parts are made from metals other than aluminum, whereas, the remaining portions of many machines are made from aluminum.

By having to substitute heavier metals in certain portions of machinery which would otherwise be made from aluminum at least two drawbacks result. The first is that inexpensive single pieces of machinery components cannot be made and expensive piecing together of machine parts have to be carried out. The second drawback is that the more aluminum which has to be replaced by heavier metals the heavier the machinery is. This latter drawback is particularly severe in the aircraft industry.

b. Description of the Prior Art

There have been studies of the treatment of aluminum, but none have really been directed to the problem of increasing the surface hardness of aluminum alloys. On Mar. 18, 1933 Professor M. H. LeChatelier, published a paper in the "Academie des Sciences" authored by Paul Laffitte and Pierre Grandadam entitled "The Nitration of Several Metals" (pages 1,039 to 1,041). A second paper was published Aug. 1, 1936 by M. P. Laffitte, M. E. Elchardus and P. Grandadam in the "Revue de l'Industrie Minerale" No. 375, page 861, entitled "Research on the Nitration of Magnesium and Aluminum". A third paper was published in July and August 1935 in the "Ann. de Chimie" 11th series, pages 118 to 123 by Pierre Grandadam, entitled "Experiments on the Direct Oxidation of Platinum and the Nitration of Several Metals" (Cu, Al, Mg, Zn, Fe Ni, Ti). In all three of these publications experiments were described as the effect of nitrogen and ammonia at high temperatures on pure aluminum wire. No mention at all is made in these publications with respect to cast aluminum alloys or to cast and mechanically worked aluminum alloys or to the use of sources of cyanide ions as I employ in my invention. A fourth publication is one published by the German Company Degussa in December 1970 and authored by Bruno Finnein entitled "Wear Resistant Surfaces by Treating Titanium and Titanium Alloys in Salt Baths". In this publication titanium or its alloys are treated with salt baths containing cyanide ions at a temperature of 800°C. Of course, experiments with titanium bear no relationship with respect to aluminum and, in addition, the use of temperatures in the range of 800°C could not possibly be used on aluminum alloys. Two other reasons explain why the Degussa article bears no teaching whatsoever with regard to aluminum alloys. This Degussa article does not inform one of the compositions of the bath but merely states that carbon and nitrogen form mixed crystals with titanium, which seems entirely doubtful to me. My opinion is that vanadium carbides and aluminum nitrides may be formed and these compounds may be responsible for the formation of a deep layer. Degussa, however, stages that the composition of the layer is unknown. Further in our case, I know that silicon, magnesium and nickel are necessary. The difference between treatment of titanium and treatment of aluminum appears to mainly consist in that the hard layer, in the case of aluminum, is mostly produced by alloy constituents of the interior of the Al alloy, such as silicon, whereas the hard layer of the titanium alloy is formed by direct reaction between the bath and the surface of the Ti alloy and there appears to be no migration of constituents from the interior to the surface.

SUMMARY OF THE INVENTION

In accordance with this invention there is provided a cast alloy of aluminum or a cast and mechanically worked alloy of aluminum containing substantial quantities of silicon, copper, nickel and magnesium and, optionally, small quantities of iron, titanium manganese, zine and chromium, characterized by Vickers surface hardness of about 250 kg/mm² to about 1,400 kg/mm², depending on the composition of the alloy and its treatment. This is to be contrasted with a Vickers surface hardness for the untreated aluminum alloy in the range of 100 kg/mm².

This increased surface hardness of said aluminum alloys is effected by treating said aluminum alloy with a source of cyanide ion at a temperature of 450° to 550°C. The alloying elements content in the aluminum alloys which can be treated by the process of this invention are those having the composition:

- Si % 0.2 to 30.0
- Cu % 0.2 to 5.6
- Ni % 0.2 to 6.0
- Mg % 0.2 to 5.0
- Fe % 0.0 to 1.0
- Ti % 0.0 to 0.2
- Mn % 0.0 to 1.5
- Zn % 0.0 to 2.0
- Cr % 0.0 to 0.7

The usual source of cyanide ion is sodium cyanide. Other cyanide sources can be used, for example, potassium cyanide.

The temperature at which the aluminum alloy is kept in contact with the source of cyanide is preferably at about 450° to 550°C. At this temperature a time of exposure of the aluminum alloy to the cyanide source is preferably for a period of time of preferably from about 8 to about 12 hours.

In the heating time there is about one half hour incubation. Times longer than 20 hours do not seem to be practical due to the parabolic relationship of time X depth of the layer. Shorter times in the order of about 4 hours treatment showed good results and a smaller surface layer depth resulted but it had the same hardness as with longer treatments. Furthermore, the zone behind this layer is not completely depleted of silicon crystals. This fact is very important from the point of view of the hardness gradient from the surface to the
Studies of the treated alloys were conducted. A review of the micrographs of the treated alloys indicated the growth of an oxide layer simultaneous with the development of the hard particle layer. X-Ray diffraction studies were conducted on the surface of treated alloys 124 and 138. The results showed that the surface of the treated alloys were coated with a spinel type oxide having a lattice parameter of 8.07A ±0.2A. Two compounds, NiAlO₄ (8.05A) and MgAl₂O₄ (8.08A) are potential matches for the data, but electron microprobe data showed that the oxide contains Mg. Thus, MgAl₂O₄ is the major constituent in the oxide layer. This layer contains numerous metallic particles which have been identified as Al₂Ni by X-ray diffraction which was consistent with microprobe data showing that these particles contain Ni. Also, the diffraction pattern and microprobe data show elemental Si to be present in the oxide layer. There was no indication of the oxidation of either Si or Ni.

In practice the cast aluminum alloy or cast and mechanically worked aluminum alloy was immersed partially or completely in the salt bath for the period of time and, after the exposure was completed, it was convenient to rinse the test piece with water. Hardness tests were then run on the treated aluminum surfaces utilizing the Vickers hardness test E: 92-55 as described in the 1955 Book of ASTM Standards, Part 1, Ferrous Metals, published by the American Society for Testing Materials, 1916 Race Street, Philadelphia, Pa., at pages 1694 to 1699, hereafter referred to as Vickers Hardness. The magnitude of the test load used was 35 grams.

In preparing the salt bath, it is convenient to mix with the cyanide salt fluxes or other auxiliary agents which enable the salt bath to be kept conveniently at the 450° to 550°C. temperature. Examples of such agents are the use of boron oxide or the use of a mixture of sodium hydroxide and sodium carbonate. These auxiliary agents do not enter into the reaction and merely permit the cyanide ion to be brought into a convenient form at the 450° to 550°C. range in contact with the aluminum alloy.

THEORY OF THE PROCESS

While I do not want the interpretation of the claims for my invention to be restricted in any manner by any theory it seems that the phenomenon of surface hardness is connected with the migration of silicon from the interior to the surface, leaving behind the surface a zone of lower silicon content. The mobility of silicon atoms increases with the silicon content to a maximum of approximately 18 (e.g., alloy 138). With a further increase of silicon content this mobility decreases as for example with alloy 244 which has a silicon content of about 24. In addition to the silicon migration, the surface hard layer appears to comprise some Al₂Ni. Although the increase of hardness appears to be due mainly to the increase in silicon content in the hard surface layer, the hardness of alloy Y must be considered from a different point of view. The silicon content of the Y alloy is only 0.5 percent and consequently there is no essential migration of silicon. The hardness of the surface layer of the Y alloy can be attributed mostly to the formation of MgAl₂O₄, which presumably occurs as a result of oxidation during the salt bath treatment.

Obviously a combination of concentrating silicon and/or Al₂Ni on the surface, as well as, the formation of MgAl₂O₄ can occur to produce the surface hardness of the aluminum alloy as a result of the treatment of this invention. In addition, other undiscovered effects may occur.

That there are several different particles in the hard layer is really a very favorable aspect as far as wear resistance is concerned. Different hardness is parallel to different elasticity, which reduces the danger of removing brittle particles.

The oxide layer on the extreme outside has a different composition, mostly MgAl₂O₄, as compared with the hard particle layer, which consists chiefly of Si crystallites. An exposure time of merely 4 hours produces layers with less thickness but practically the same hardness. It should be pointed out that hardness is a property of the crystallites formed while thickness of the hard surface layer depends on exposure time. Wear resistance, on the other hand, depends on both these factors: increased hardness usually increases wear resistance, and greater thickness implies in longer abrasion time of the layer.

The oxide layer consists mostly of MgAl₂O₄. The oxide layer may contribute to the overall hardness; but its hardness is much below that of the Si layer. The hard layer consists of Si and some Al₂Ni. Also here Al₂Ni has a lower hardness than Si particles.

Even a short exposure time of 4 hours produces a hard layer of reduced thickness in alloys 124, 138 and 244.

Time of exposure and temperature have a certain influence on the hard layer thickness. I found a parabolic relation for dependence of thickness on exposure time:

\[ p = K \sqrt{t} \]

\( p = \) thickness in 0.001 mm  
\( K = \) constant, varying slightly between 5 and 7  
\( t = \) time in hours  

The higher the temperature is, the earlier a given hardness appears to be obtained.

The real hardness of the layer does not depend on thickness. Hardness is based on the type of particle, whether it consists of a complex magnesium-aluminum-oxide or of silicon. The apparent hardness, however, shows higher values with increased thickness of the layer, due to resistance to penetration met by the indenter for a given load.

DESCRIPTION OF THE FIGURES

FIGS. 1 through 12 and 14 and 16 are photomicrographs of the alloys treated in accordance with this invention.

FIGS. 13 and 15 are photomicrographs of untreated alloys. The data with regard to these Figures are as follows:

| FIG. 1 | Untreated - 150x | Alloy - 124 | Treatment: NaCN + 4% B₂O₃; Temperature = 530°C.; Time = 4 hours | Thickness of the hard layer = 13 microns. |
| FIG. 2 | Untreated - 150x | Alloy - 124 | Treatment: NaCN + 4% B₂O₃; Temperature = 530°C.; Time = 8 hours | Thickness of the hard layer = 18 microns. |
-continued Treatment: NaCN + 4% B2O3; Temperature = 530°C; Time = 12 hours
Thickness of the hard layer = 20 microns. FIG. 4

Unetched - 150x Alloy - 138
Treatment: NaCN + 4% B2O3; Temperature = 530°C; Time = 4 hours
Thickness of the hard layer = 8 microns. FIG. 5

Unetched - 150x Alloy - 138
Treatment: NaCN + 4% B2O3; Temperature = 530°C; Time = 8 hours
Thickness of the hard layer = 15 microns. FIG. 6

Unetched - 150x Alloy - 138
Treatment: NaCN + 4% B2O3; Temperature = 530°C; Time = 12 hours
Thickness of the hard layer = 17 microns. FIG. 7

Unetched - 150x Alloy - 244
Treatment: NaCN + 4% B2O3; Temperature = 530°C; Time = 4 hours
Thickness of the hard layer = 12 microns. FIG. 8

Unetched - 150x Alloy - 244
Treatment: NaCN + 4% B2O3; Temperature = 530°C; Time = 8 hours
Thickness of the hard layer = 14 microns. FIG. 9

Unetched - 150x Alloy - 244
Treatment: NaCN + 4% B2O3; Temperature = 530°C; Time = 12 hours
Thickness of the hard layer = 25 microns. FIG. 10

Unetched - 150x Alloy - 244
Treatment: NaCN + 4% B2O3; Temperature = 520°C; Time = 12 hours.
Thickness of the hard layer = 10 microns. FIG. 11

Unetched - 150x Alloy - 124
Treatment: NaCN + 4% B2O3; Temperature = 520°C; Time = 12 hours
The start of migration of Silicon to the surface of the test piece can be observed. FIG. 12

Unetched - 500x Alloy - 124
Treatment: NaCN + 4% B2O3; Temperature = 530°C; Time = 12 hours
Indentation of micro-hardness (35 grams)
Hardness of micro-hardness = 104 kg/mm²
Hardness of the hard layer = 1200 kg/mm² FIG. 13

Alloy - 124 Condition: as cast X120 - not etched FIG. 14

Alloy - 124 Condition: as cast X120 - not etched FIG. 15
Conditions of treatment: Bath = 90% NaCN + 3% Na2CO3 + 6% H2O Temperature = 540°C; Time = 13 hours
Thickness of the hard layer = 15 microns FIG. 16

Alloy - 138 Condition: as cast X120 - not etched FIG. 17

Alloy - 138 Condition: as cast X120 - not etched FIG. 18
Conditions of treatment: Bath = 90% NaCN + 3% NaOH + 1% Na2CO3 + 6% H2O; Temperature = 540°C; Time = 9 hours
Thickness of the hard layer = 6 microns.

FIGS. 17 and 18 show the relation of the layer thickness to the exposure time.
FIG. 19 shows the results of wear tests made with Alloy - 124.
Alloy 124 was treated for four hours at 540°C with the bath of example 8 and the friction test used ASTM test D2714-68.

DESIGN OF THE PREFERRED EMBODIMENTS

All the alloys which were employed were sand cast or cast in permanent molds or cast and mechanically worked.

Examples of the alloys used and the analysis of their contents are as follows:

<table>
<thead>
<tr>
<th>DESIGNATION</th>
<th>ALLOY 124</th>
<th>ALLOY 138</th>
<th>ALLOY 244</th>
</tr>
</thead>
<tbody>
<tr>
<td>COMPOSITION</td>
<td>Si %</td>
<td>Cu %</td>
<td>Mg %</td>
</tr>
<tr>
<td>Ni %</td>
<td>Fe %</td>
<td>0.05-0.7</td>
<td>0.05-0.7</td>
</tr>
<tr>
<td>Ti %</td>
<td>0.05-0.7</td>
<td>0.05-0.7</td>
<td>0.05-0.7</td>
</tr>
<tr>
<td>Zn %</td>
<td>0.05-0.7</td>
<td>0.05-0.7</td>
<td>0.05-0.7</td>
</tr>
<tr>
<td>Cr %</td>
<td>0.05-0.7</td>
<td>0.05-0.7</td>
<td>0.05-0.7</td>
</tr>
<tr>
<td>A1 %</td>
<td>0.05-0.7</td>
<td>0.05-0.7</td>
<td>0.05-0.7</td>
</tr>
</tbody>
</table>

These alloys are well known and are designated as indicated above or are designated by other means as shown in the following table.

<table>
<thead>
<tr>
<th>DESIGNATION</th>
<th>ALLOY 124</th>
<th>ALLOY 138</th>
<th>ALLOY 244</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASTM: B-108-55T</td>
<td>CN 42A</td>
<td>SN 122A</td>
<td>——</td>
</tr>
<tr>
<td>U.S. FEDERAL GOVERNMENT SPECIFICATION</td>
<td>QQQ-A1596b-class 3</td>
<td>QQQ-A1596b-class 9</td>
<td>——</td>
</tr>
<tr>
<td>COMMERCIAL DESIGNATION</td>
<td>142</td>
<td>142</td>
<td>4222 (sand cast)</td>
</tr>
<tr>
<td>S.A.E.</td>
<td>39</td>
<td>39</td>
<td>——</td>
</tr>
<tr>
<td>A.M.S.</td>
<td>——</td>
<td>——</td>
<td>——</td>
</tr>
<tr>
<td>DIN - 1725</td>
<td>——</td>
<td>——</td>
<td>1761</td>
</tr>
<tr>
<td>ALCAN</td>
<td>218</td>
<td>6207</td>
<td>3210</td>
</tr>
<tr>
<td>Nural</td>
<td>1761</td>
<td>——</td>
<td>1761P</td>
</tr>
<tr>
<td>DIN - 1725</td>
<td>——</td>
<td>——</td>
<td>——</td>
</tr>
</tbody>
</table>

The above four types of alloys were subjected to the exposure of cyanide ions by immersing the alloy partially or completely into the appropriate salt bath, for a period of time of 8 to 12 hours at a temperature of 500° to 530°C. After the exposure the test piece was rinsed with water and the hardness of the treated surface at several areas was determined.

EXAMPLES 1 - 7

Examples of salt baths employed are as follows:

SALT BATH A
98 percent By weight of sodium cyanide and 2 percent by weight of boron oxide (B2O3).

SALT BATH B
90 percent By weight of sodium cyanide, 3 percent by weight of sodium hydroxide, 1 percent by weight of sodium carbonate and 6 percent by weight of water vapor.

The results achieved with the treated alloys after rinsing with water are set forth below and stated in Vickers Hardness (HV) in kg/mm². The hardness of untreated aluminum alloy (HV) is 110 to 120 kg/mm².
**EXAMPLE 8**

In another test Alloy 124 and Alloy 138 were treated as described above for Examples 1 to 7 with a bath containing the following composition:
- 49 percent by weight of sodium cyanide
- 49 percent by weight of potassium cyanide
- 2 percent by weight of boron oxide ($B_2O_3$)

The Vickers Hardness (HV) in kg/mm² for Alloy 124 and Alloy 138 treated at 550°C for 9 hours are as follows:

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Bath A</th>
<th>Bath B</th>
</tr>
</thead>
<tbody>
<tr>
<td>124</td>
<td>HV (kg/mm²)</td>
<td>HV (kg/mm²)</td>
</tr>
<tr>
<td>580</td>
<td>670</td>
<td>820</td>
</tr>
<tr>
<td>1000</td>
<td>820</td>
<td>960</td>
</tr>
<tr>
<td>740</td>
<td>960</td>
<td>700</td>
</tr>
<tr>
<td>900</td>
<td>700</td>
<td>630</td>
</tr>
<tr>
<td>1010</td>
<td>630</td>
<td>970</td>
</tr>
</tbody>
</table>

We claim:

1. A process for increasing the surface hardness of cast or cast and mechanically worked aluminum alloys wherein said aluminum alloy has the following alloying element content:
- Si % 0.2 to 30.0
- Cu % 0.2 to 5.6
- Ni % 0.2 to 6.0
- Mg % 0.2 to 5.0
- Fe % 0.0 to 1.0
- Ti % 0.0 to 0.2
- Mn % 0.0 to 1.5
- Zn % 0.0 to 2.0
- Cr % 0.0 to 0.7

which comprises immersing said aluminum alloy into a molten source having a major amount of cyanide at a temperature of about 430°C to 550°C for a period of time of at least about one-half hour.

2. A process according to claim 1, wherein said aluminum alloy has the following alloying element content:
- Si % 11 to 13
- Cu % 0.8 to 1.5
- Ni % 0.8 to 1.3
- Mg % 0.8 to 1.3
- Fe % < 0.7
- Ti % < 0.2
- Mn % < 0.2
- Zn % < 0.2
- Cr %
- A1 % 82 to 85.

3. A process according to claim 1, wherein said aluminum alloy has the following alloying element content:
- Si % 17 to 19
- Cu % 0.8 to 1.3
- Ni % 0.8 to 1.3
- Mg % 0.8 to 1.3
- Fe % < 0.7
- Ti % < 0.2
- Mn % < 0.2
- Zn % < 0.2
- Cr %
- A1 % 76 to 80.

4. A process according to claim 1, which comprises using as a cyanide source a bath of 98% sodium cyanide and 2 percent boron oxide.

5. A process according to claim 1, which comprises using as a cyanide source a melt of 90 percent sodium cyanide, 3 percent sodium hydroxide, 1% sodium carbonate and 6 percent water.

6. A process according to claim 1, which comprises carrying out the treatment for a period of 8 to 12 hours.

7. A process according to claim 1, wherein the surface hardness is increased from about 250 kg/mm² to about 1400 kg/mm².

8. A process according to claim 1, wherein said alloying element content:
- Si % 11 to 13
- Cu % 0.8 to 1.5
- Ni % 0.8 to 1.3
- Mg % 0.8 to 1.3
- Fe % 0.0 to 1.0
- Ti % 0.0 to 0.2
- Mn % 0.0 to 1.5
- Zn % 0.0 to 2.0
- Cr % 0.0 to 0.7

which comprises immersing said aluminum alloy into a molten source having a major amount of cyanide at a temperature of about 430°C to 550°C C. for a period of time of at least about one-half hour.