Surface Hardening Technology for Aluminum Alloy by Plasma Arc Alloying Process†

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Abstract

To improve the wear resistance of Al alloy, a new surface hardening process has been developed by employing the plasma arc alloying process, which is one of the surface melting and alloying processes, and enables the formation of a thick hardened layer of millimeter order thickness on Al alloy surfaces by alloying metals and ceramic powders into a molten pool. Structure, hardness, and wear resistance of an alloyed layer were evaluated for various kinds of metals and carbides as alloying materials, and suitable alloying materials are discussed.

KEY WORDS: (Aluminum) (Wear) (Hardness) (Surface hardening) (Plasma arc) (Alloying) (Composite) (Ceramics) (Powder)

1. Introduction

Al alloys have become important materials as components for weight-saving in industrial products, especially in transport systems such as automobile, railroad rolling stock, high speed ferryboats, aircraft and aerospace industries so on. In addition, Al alloy is quite a suitable material to establish the recycling systems for industrial products. One of the major drawbacks, however, in the characteristics of Al alloy is poor wear resistance in comparison with steels. To improve this, anodizing and some metallic platings are available, but due to thin layer less than several ten microns, their applications are limited. Therefore, a surface hardening technology with much thicker layer has been required for Al alloy components resisting severe wear condition. In 1995, the Japan Research and Development Center for Metals published a review "Thick Surface Hardening Technology for Aluminum Alloys", in which the state of research and development in this field was outlined.

In this paper, typical methods for providing hardening of a thick surface layer of the order of a millimeter of Al alloy surface and, in particular, the plasma arc alloying technique will be considered.

2. State-of-The-Art of Surface Hardening Technology for Al Alloys

† Received on May 31, 2000
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In order to weight-save the products, replacing iron-based parts by Al-based parts is a reasonable process; this in many cases requires the hardening of the surface layer. Examples related to the automobile industry are given in Table 1. Required thicknesses are large, more than 0.5 mm to 5 mm and hardness is around HV 200 - 400 and much higher ranges. These requirements are not available by conventional anodizing and plating processes. Moreover, this requirement for the hardening treatment is prompted not only by an improvement of the wear resistance but also in many cases by the multifunctioning conditions.

Fig. 1 shows the relation between the hardness and the thickness of improved surface layers by respective surface hardening processes that are described in reference works. The relationships between these two parameters are indicated by the letter "L." and respective processes can be subdivided into two groups.

Namely, the first group comprises processes that provide a high hardness of HV 800 - 1000, but in a thin surface layer around 0.1 mm thickness in maximum and belong to techniques designed for coating the surface of Al alloys with hard materials. There are the thermal spraying process (S) and the conventional anodizing and the plating process (P). The increased layer thickness is required due to the rather weak substrate in case of severe wear conditions as already shown in Table 1. To increase
Table 1 Required characteristics of surface hardened Al components of automobile.

<table>
<thead>
<tr>
<th>Automobile part</th>
<th>Hardened layer</th>
<th>Other characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Thickness, mm</td>
<td>Hardness HV</td>
</tr>
<tr>
<td>Cylinder head</td>
<td>3~5</td>
<td>200~300</td>
</tr>
<tr>
<td>Piston</td>
<td>1~2</td>
<td>300~400</td>
</tr>
<tr>
<td>Rocker arm</td>
<td>0.5 and above</td>
<td>500~800</td>
</tr>
<tr>
<td>Camshaft</td>
<td>Over 1</td>
<td>Over 700</td>
</tr>
<tr>
<td>Connecting rod</td>
<td>1~2</td>
<td>Over 700</td>
</tr>
<tr>
<td>Engine valve</td>
<td>Over 1</td>
<td>Over 700</td>
</tr>
<tr>
<td>Oldham's ring</td>
<td>0.5</td>
<td>200~400</td>
</tr>
</tbody>
</table>

Table 2 Characteristics of heat sources used for surface fusion and alloying process.

<table>
<thead>
<tr>
<th>Process</th>
<th>Power density W/mm²</th>
<th>Max. thickness of hardened layer</th>
<th>Level of thermal effect</th>
<th>Condition of alloying materials</th>
<th>Atmosphere condition of treatment</th>
<th>Device cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>TIG arc (TIG)</td>
<td>~150</td>
<td>About 5mm</td>
<td>High</td>
<td>Rod, Solid wire, Cored wire</td>
<td>Atmospheric pressure</td>
<td>Low (1~2 million yen)</td>
</tr>
<tr>
<td>MIG arc (MIG)</td>
<td>~150</td>
<td>About 10mm</td>
<td>High</td>
<td>Solid wire, Cored wire</td>
<td>Atmospheric pressure</td>
<td>Low (1~2 million yen)</td>
</tr>
<tr>
<td>Plasma arc (PTA)</td>
<td>~1000</td>
<td>About 20mm</td>
<td>High</td>
<td>Rod, Wire, Powder</td>
<td>Atmospheric pressure</td>
<td>Fare (10~20 million yen)</td>
</tr>
<tr>
<td>Electron beam (EB)</td>
<td>Over 10000</td>
<td>About 20mm</td>
<td>Low</td>
<td>Rod, Wire, Pre-coating</td>
<td>High vacuum</td>
<td>High (100~200 million yen)</td>
</tr>
<tr>
<td>Laser beam (LB)</td>
<td>Over 10000</td>
<td>Several mm</td>
<td>Low</td>
<td>Rod, Wire, Powder, Pre-coating</td>
<td>Atmospheric pressure</td>
<td>High (100~200 million yen)</td>
</tr>
</tbody>
</table>

The layer thickness, an improvement of the adhesion strength of coated layer to a substrate is indispensable for preventing a peeling of the coated layer along with a requirement to increase layer deposition rate. These problems requires future studies.

The second group comprises processes that provide rather easily a thick surface layer of an order of millimeter with comparatively low hardness around HV200 and belong to surface alloying by fusion techniques. Such processes, most of them are tentative and under development, consist of the local fusion of the surface of Al alloys, the addition of alloying materials to the molten pool, and the formation of alloyed and composite layers on the treated surface. Since fusing the surface is local within a required depth, a heat source used for a high-energy density welding is used. This source can be TIG arc (TIG), a MIG arc (MIG), a plasma arc (PTA), a laser beam (LB), or an electron beam (EB). Comparison of the properties of heat sources is given in Table 2. The heat source with high energy density is capable of controlling the depth of fusion of the substrate surface and provides a high process speed with less heat damage to the substrate. A control of the structure of the alloyed layer is very important to ensure a high hardness of the layer, and from

Fig.1 Relation between hardness and thickness of surface hardened layer of Al alloys.
a practical point of view, the surface finishing of a hardened layer is indispensable to make it smooth.

3. Plasma Arc Alloying Process

3.1 Process

Plasma arc alloying process is a convenient process to synthesis various kinds of alloyed and composite layers by using metal and ceramic powders as the admixtures along with good controllability of the depth of fusion of the substrate surface due to comparatively high energy density. Fig. 2 shows the schematic illustration of the plasma arc alloying system. The plasma arc process provides local fusion to a depth up to 20 mm on the surface of Al alloy substrate (base metal) and simultaneously metal and ceramic powders are supplied by passing through the plasma arc into the fusion zone. In this case, it is possible to continuously form the alloyed and composite layers on the substrate surface from some mm up to 20 mm in thickness by traveling the plasma torch on the substrate.

Table 3 Hardness of typical Al-base intermetallic compounds, aluminides.

<table>
<thead>
<tr>
<th>Compound</th>
<th>HV &lt; 500</th>
<th>500 ≤ HV &lt; 700</th>
<th>700 ≤ HV</th>
</tr>
</thead>
<tbody>
<tr>
<td>AuAl7</td>
<td>190–240</td>
<td>500–600</td>
<td>650–750</td>
</tr>
<tr>
<td>CoAl11</td>
<td>400–600</td>
<td>500–700</td>
<td>800</td>
</tr>
<tr>
<td>CrAl5</td>
<td>400–500</td>
<td>540–550</td>
<td>700–800</td>
</tr>
<tr>
<td>FeAl</td>
<td>340–440</td>
<td>490–510</td>
<td>800–900</td>
</tr>
<tr>
<td>MgAl2</td>
<td>350–430</td>
<td>530–630</td>
<td>900–1000</td>
</tr>
<tr>
<td>NiAl</td>
<td>320–420</td>
<td>500–600</td>
<td>1100</td>
</tr>
<tr>
<td>ScAl</td>
<td>250–350</td>
<td>530–630</td>
<td>700–800</td>
</tr>
<tr>
<td>TiAl</td>
<td>170–240</td>
<td>400–600</td>
<td>427–740</td>
</tr>
</tbody>
</table>

3.2 Metal powder addition

Metal powder added into a molten pool reacts with molten aluminum and forms an alloyed layer, in which structure depends basically on the phase diagram of aluminum with the metal added\textsuperscript{33}. Hardness increase of the alloyed layer is achieved mainly by the formation of hard intermetallic compounds as shown in Table 3, which shows typical aluminides.

Fig. 3 shows a schematic illustration of typical structures of the alloyed layer observed for the respective metals by testing many different metal powders. Homogeneous structure is easy to form in the case of metals having eutectic reaction with aluminum and whose liquidus temperature is comparatively low. However, metals such as chromium and titanium, having peritectic and monotectic reactions with aluminum and with a high liquidus temperature are likely to form a compound layer in the upper part of the fusion zone and are unlikely to form an uniform alloyed layer unless the amount of metal added is small enough. In the case of eutectic-peritectic reaction with, for example, nickel, the structure of the alloyed layer is in the intermediate condition.

![Fig. 2 Schematic illustration of plasma arc alloying process.](image)

![Fig. 3 State of the alloyed layers formed by adding metal powders](image)
Surface Hardening Technology for Aluminum Alloy by Plasma Arc Alloying Process

Fig. 4 Typical microstructure of the alloyed layer in cross-section, (a) Si, (b) Ti.

Fig. 5 Effect of content of alloying element on hardness of the alloyed layer.

Fig. 6 State of composite layers formed by adding ceramics powders.
Furthermore, in the case of tantalum and tungsten, the melting points of which are above 3000 centigrade, the reaction with molten aluminum hardly occurs due to the comparatively low temperature of molten aluminum and a rapid cooling rate. This results in a composite structure with dispersed metal particles in a bottom part of the fusion zone.

Fig. 4 shows typical microstructure of the cross-section of the alloyed layer.

Fig. 5 shows the relation between the content of the alloyed element in the alloyed layer and the hardness. The hardness increases with increasing content of the alloyed element, irrespective of the type of the alloyed element. This corresponds mainly to the increase of the volume fraction of intermetallic compounds formed, which results in the formation of large compound lumps or layers. Since intermetallic compounds are inherently brittle, however, cracks are likely to occur in these large compound lumps or layers under the action of tensile residual stress generated during cooling of the alloyed layer. Experimental results obtained so far show that at a hardness above HV 300, a crack occurs in the alloyed layer indicated as a filled mark in Fig.5, irrespective of the kind of added element. Thus an increase of hardness by the addition of metals has a limit. The observations of the structure of the alloyed layer and the resulting hardness show that among metal elements copper and silicon are the most effective. In the alloyed layer formed in this case, CuAl₂ and Si, which are hard particles, are uniformly dispersed in the aluminum matrix and such alloyed layers show an excellent resistance to cracking.

3.3 Ceramic powder addition

The supply of ceramic particles to the fusion zone makes it possible to form a ceramic particle dispersed layer on the surface of an Al alloy. A schematic illustration of the structure of a cross-section of a composite layer is shown in Fig.6. Until now, the authors used carbides, nitrides, borides, oxides and silicides as composite powders in their tests and classified the structure of resulted composite layers into five basic types shown in Fig.6.

Ceramic powders with a melting point of higher than 2500 centigrade form a composite layer with the Al matrix without melting as shown in Type I to III. Most
carbides belong to these types. In the other type, in the case of particles of lower melting point ceramics, particles such as Cr$_3$C$_2$ and TiSi$_2$ react readily with aluminum and form a compound layer as type IV, which mainly consists of aluminides. Particles, such as TiO$_2$ do not react with aluminum and pile up on the surface in the form of slag without mixing with molten aluminum as shown in type V.

Fig. 7 shows the microstructure of the cross-section of composite layers formed in the case of carbide particles, in which the structures of type I to III are observed. The structure of composite layers are controlled not only by the density of particle but also the size of particle as shown in Fig. 8 indicating the dispersion condition of particles.

Fig. 9 shows the relation between the TiC volume fraction and the hardness of TiC particle composite layers. The relation between these two parameters practically follows a rule of particle-dispersion type composite formation and the hardness shows a sharp increase when the TiC volume fraction exceeds about 50%.

3.4 Simultaneous addition of metal and ceramic particles

Metal powder addition enables the formation of alloyed layers with hardness of HV 500 ~700, but their drawback is a frequent occurrence of cracks. Therefore, it is rather difficult to achieve the crack free layer at hardness above HV 300. The application of ceramic material additives needs a high volume fraction of ceramic particles to get high hardness due to the weak aluminum matrix strength. Therefore, it becomes necessary to strengthen the aluminum matrix to raise the hardness and wear resistance property. This can be effectively achieved by adding metal and ceramic material additives simultaneously.

Specifically, this method allows formation of hybrid layers containing both additives. The addition of metal additives allows the formation of a uniform alloyed layer, thus strengthening the aluminum matrix, and the hard ceramic particles added act as the dispersed particulate.

A typical microstructure of a hybrid layer obtained by the simultaneous addition of copper as a metal additive and TiC as a ceramic material additive is shown in Fig. 10. In the photo, black-looking large particles are TiC and white, rod-shaped compounds surrounding these particles are the $\theta$ (CuAl$_2$) phase. The gaps between these two phases are completely filled with eutectic structure consisting of $\theta$ and $\alpha$-Al. In this case, the

Fig. 10 Microstructure of Cu-TiC composite layer.
The resulting structure is rather dense; therefore its hardness reaches HV 550 and cracking does not occur.

Fig. 11 shows the comparison between the wear resistance of such hybrid layers and those of layers consisting of copper or TiC alone. The evaluation of wear was done by Ogoshi-sliding wear test, in which a rotating counter roller pressed on the surface of the layer at a constant load. The addition of copper and TiC alone improved the wear resistance of base aluminum by about ten times, almost the same level as mild steel, SS400 and austenitic stainless steel, SUS304. However, an improvement to a level above that has not been achieved. In contrast, the composite addition results in a much more rise in the wear resistance by an order of magnitude and the resulting wear resistance is about 100 and more times higher than that of base aluminum.

![Image of Al-Cu:48mass%Cu TiC:Vol%:60% (3passes)](image)

**Fig. 11** Comparison between wear volume of layers (Cu, TiC, Cu+TiC), pure Al base, and ferrous metals (mild steel SS400, stainless steel SUS304) evaluated by Ogoshi-type sliding wear test.

4. **Application in Practice**

As well as in the automobile industries, research and development of surface hardening technology of aluminum is also ongoing with the purpose of improving the wear resistance and partial strengthening of aluminum alloy products such as vacuum vessels, dies, flanges, screw units, and joint surfaces that operate under high surface pressure, high load conditions, and to improve the resistance to adhesion of the sliding surface and of sliding components. An example of the thick layer hardening of flanges made of Al alloy is shown in Fig. 12. In this case, a manual TIG arc welding technique is used to deposit the alloyed layer by using an aluminum-copper alloy filler rod as shown on the left-side photo in the as-deposited condition. The resulting alloyed layer has a hardness of about HV 250 and is easily machined as shown on the right-side photo. Another application is the partially strengthened screw hole made by using an electron beam welding (EB) technique as shown in Fig. 13. In this case, copper wire was used as an alloying material. A dark-etched region is the alloyed area, in which screw holes were machined after alloying.

5. **Conclusions**

The thick layer surface hardening technology for Al alloy is still in the stage of development and examples of its application to actual machine parts are scarce. As wear resistance and lubrication properties of aluminum alloys are insufficient, they have been so far excluded from application to designing machine parts. However, the
technology discussed in this work allows looking at aluminum alloys from a new perspective and considers it to be a lightweight material with new surface functions. The description of processes that have not been discussed in this work can be found in reference works.

Acknowledgment

Advice to this work from Emeritus Professor, F. Matsuda, Osaka University, were greatly appreciated.

References