Formation of TiC/Ti₂AlC Composite Layer and Improvement on Surface Roughness

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In order to improve surface hardness, surface modification of die casting aluminum alloys was carried out by applying a new method called Electrical Discharge Alloying with ultrasonic vibrations, in which a conventional electrical discharge machine can be used. The layer deposited on the substrate consists of TiC and Ti₂AlC formed by the reaction between titanium contained in the green compact electrode, the aluminum in the electrode and the substrate and also the carbon decomposed from a working fluid. When the ultrasonic vibration is applied to the substrate, especially at a frequency of 94.2 kHz, the discharged craters are bigger than those obtained when alloying without ultrasonic vibration. Also, for single discharge, the amount of deposited Ti and C increases near the edge of the crater. When the ultrasonic vibration is applied to the electrode for single discharge, many convex-shaped craters are generated on the substrate. The cross-sectional hardness of the alloyed area increases with increase in the concentration of carbon and titanium. The secondary elaboration using the cast Ti–36 mass%Al solid electrode is effective for the improvement of surface roughness of the modified layer. When the green compact electrode is used in the primary Electrical Discharge Alloying and the cast solid electrode is used in the secondary elaboration, surface roughness is not so different between the process with and that without ultrasonic vibration. However, the modified layer’s thickness obtained with ultrasonic vibration is thicker than that without ultrasonic vibration.

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1. Introduction

Aluminum and aluminum alloys are materials that exhibit excellent characteristics such as, good workability and low density. In recent years, these materials have been used in fields where components require light weight coupled with the high strength of some aluminum alloys such as in construction of strong light weight structures that are particularly advantageous for anything that automobiles, railways, ships aircrafts and electronic equipments. However, the wear resistance of aluminum alloys is inferior to that of steel. If the wear resistance of aluminum can be improved to match or better that of steel, aluminum can be substituted for steel in most and various other fields of applications requiring lightweight materials. Surface hardening methods for aluminum alloys are mostly divided into two main categories, which are:

1. Surface coating, which covers hard surface materials. PVD, CVD, plating,1,2 spraying,3,4 etc. fall in this category.
2. Alloying method, which makes the surface melt. Alloying elements or ceramics are purchased. Hard anodizing,5 laser alloying6,7 and plasma transferred arc welding8 fall in this category.

However, though it is possible to form a hard coating layer by the coating methods, it is difficult to form a thick film. Also, the rate of film formation is slow except for the spraying, and the adhesion with aluminum substrate is low. Except for the hard anodizing, though it is possible that the alloying methods make a thick film, the hardness of the layer is not high enough. Moreover, in order to prevent the occurrence of cracks at the interface between the modified layer and the substrate, when the hard film in which thermal expansion coefficient differ from the substrate is formed, gradation composition is required in both methods. We have proposed an original new surface modification method of aluminum alloys using a conventional electrical discharge machine, in which the dissolved electrode materials are reacted and transferred through successive pulsed discharged arcs between an electrode and substrate.9,10 The modified surface layers are in situ composites containing TiC precipitates. It has been reported that the modified layer’s thickness can be increased by using green compact electrodes instead of solid electrodes.12 The volume fraction of TiC can also be controlled by changing the discharge conditions such as the pulse width, the discharge current and the process time. Consequently the hardness of modified aluminum surfaces can be varied at any value between 400 and 1100 HV.10 When aluminum matrix composites is used as a substrate and silicone oil is used as a working fluid, the surface hardness can be changed in the range of 700–1400 HV, by controlling the volume fraction of TiC.11 This process is referred to as Electrical Discharged Alloying (EDA). EDA has the following advantages:

1. It can be applied for electrically conductive substrate material.
2. A hard and thick modified layer can be obtained in a relatively short time.9,10
3. The adhesion of the modified layer is good, since the substrate surface is melted in the process.
4. By selecting the electrode material and the working fluid, the modified layer’s composition is easily controllable.10
5. Since only a localized heating of the surface is involved, the dimensional change of the work piece is negligible.

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In this study, titanium (Ti) powder and aluminum (Al) powder based green compacts were used as electrodes, and die casting aluminum alloy (JIS-ADC12) was used as a substrate. A modified layer, which consisted of Ti from the electrode, Al from the electrode and substrate, and carbon (C) from the working fluid was formed on ADC12 substrate by EDA.

2. Experimental Procedures

Schematic illustrations of the EDA equipments are shown in Fig. 1 and Fig. 2. A conventional electrical discharge machine is used for the surface modification of die casting aluminum alloy (JIS-ADC12) with a thickness of 5 mm. In both equipments, when a discharge is generated in the working fluid between the electrode and the substrate, EDA can be achieved. In Fig. 1, an ultrasonic vibration with a frequency of 28.8 kHz or 94.2 kHz is applied in the perpendicular direction on the substrate. Whereas in Fig. 2, an ultrasonic vibration with a frequency of 26.1 kHz or 102 kHz is applied on the electrode surface. The ultrasonic vibration is generated by supplying a sine wave, which is oscillated through the function generator and powered by the power amplifier. This ultrasonic vibration is amplified by a step horn, and propagated to the substrate or the electrode. In electrical discharge machining, workability is computed from the product of melting point and thermal conductivity. In electrical discharge machining this value must be low in order to easily machining. Therefore, copper with its high thermal conductivity is often used as electrode where low electrode consumption is required. However, in EDA, high electrode consumption rate is required, since it is necessary to transfer the electrode material to the substrate. Therefore a green compact electrode was used to take advantage of its high electrode consumption rate. The apparent thermal conductivity of the green compact electrode is lower than that of solid electrode owing to the presence of a large number of pores, so it is consumed. Crushed Ti powder (99.4 mass%) and atomized Al powder (99.8 mass%) with a powder size of less than 22 μm were used for the green compact electrode. The pre-mixture powder of Ti/36 mass%Al was pressed at 392 MPa to mold electrodes with a diameter of 16 mm. Cast Ti–36 mass%Al solid electrode with 16 mm diameter and 2 mm thickness or the green compact electrode with 16 mm diameter and 2 mm thickness was used for the secondary elaboration for improving surface roughness. The electrode polarity was negative as against that in conventional electrical discharge machining. Kerosene was used as a working fluid. Actual discharge conditions, such as discharge current (I_p), gap voltage (E_g), pulse width (τ_p) and duty factor (D_t) were recorded with a current transformer and a storage-type oscilloscope. Typical E_g and I_p waveforms during the process are shown in Fig. 3. The apparent D_t is calculated as $D_t = \frac{\tau_p}{\tau_p + \tau_s}$, where \(\tau_s\) is rest time in a pulse cycle. The fundamental process parameters in electrical discharge alloying are shown in Table 1. Elemental distribution in the cross-section of the modified layers and element transfer on the substrate were examined by elec-

![Fig. 1 Schematic diagram of an electrical discharge alloying with ultrasonic vibration on substrate system.](image1)

![Fig. 2 Schematic diagram of an electrical discharge alloying with ultrasonic vibration on electrode system.](image2)

![Fig. 3 Typical gap voltage, discharge current and ultrasonic vibration amplitude profiles recorded by a current transformer and storage scope. Process parameters: \(I_p = 15 A, E_g = 150 V, \tau_p = 256 \mu s\) and \(D_t = 0.33\).](image3)
Table 1 Process parameters in electrical discharge alloying.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gap voltage (V)</td>
<td>$E_g$</td>
</tr>
<tr>
<td>Pulse width (µs)</td>
<td>$\tau_p$</td>
</tr>
<tr>
<td>Discharge current (A)</td>
<td>$I_p$</td>
</tr>
<tr>
<td>Duty factor</td>
<td>$D_p$</td>
</tr>
<tr>
<td>Working time (s)</td>
<td>$t_w$</td>
</tr>
<tr>
<td>Electrode forming pressure (MPa)</td>
<td>$P_e$</td>
</tr>
<tr>
<td>Ultrasonic vibration frequency (kHz)</td>
<td>$f_r$ on substrate $28.8, 94.2$ on electrode $26.1, 102$</td>
</tr>
<tr>
<td>Premixture of electrode</td>
<td>Ti-36mass%Al</td>
</tr>
<tr>
<td>Electrode polarity</td>
<td>Negative</td>
</tr>
<tr>
<td>Substrate</td>
<td>JIS-ADC12</td>
</tr>
</tbody>
</table>

![Characteristic X-ray images of EPMA showing the distribution of Ti and C in crater of single discharged arc, upper: Ti-Kα images, lower: C-Kα images. Process parameters: $I_p = 15$ A, $E_g = 150$ V and $\tau_p = 256$ µs.](image)

![Typical optical micrograph showing a cross-sectional microstructure of the modified layer (etched by 5 vol%HF aqueous solution). Process parameters: $I_p = 15$ A, $E_g = 150$ V, $t_w = 180$ s and $D_p = 0.33$ and $t_w = 300$ s.](image)

Fig. 4 The effects of ultrasonic vibration and pulse width on the average crater diameter of single discharge arc.

Fig. 5 Characteristic X-ray images of EPMA showing the distribution of Ti and C in crater of single discharged arc, upper: Ti-Kα images, lower: C-Kα images. Process parameters: $I_p = 15$ A, $E_g = 150$ V and $\tau_p = 256$ µs.

Fig. 6 Typical optical micrograph showing a cross-sectional microstructure of the modified layer (etched by 5 vol%HF aqueous solution). Process parameters: $I_p = 15$ A, $E_g = 150$ V, $t_w = 180$ s and $D_p = 0.33$ and $t_w = 300$ s.

3. Results and discussion

3.1 The effect of the ultrasonic vibration on substrate

The peak-to-peak amplitudes of the ultrasonic vibration at the center of the substrate are 9.3 and 0.6 µm at resonant frequency of 28.8 and 94.2 kHz respectively. The effects of the ultrasonic vibration frequency ($f_r$) and $\tau_p$ on the single discharge crater diameter ($d_c$) are shown in Fig. 4. In this figure, it is shown that $d_c$ increases with $\tau_p$ or $f_r$. Using XRD, TiC was identified in the single discharge arc’s crater. The distribution of Ti and C in the crater is shown in Fig. 5. When the ultrasonic vibration is applied to the substrate, especially at a frequency of 94.2 kHz, generated craters are bigger than those obtained without the ultrasonic vibration. Also, deposited Ti and C concentrations increase around the crater edge. Therefore TiC concentration is higher around the crater edge. A typical optical micrograph of the modified layer’s cross-section with an average thickness of approximately 55 µm, is shown in Fig. 6. The microstructural change in the morphology of the modified layer obtained from repeated constituent elements transfers from the green compact electrode and the working fluid, cannot be fully recognized because of micrographs low magnification. The effects of $f_r$ and $\tau_p$ on the modified layer’s thickness ($d_m$) for a process time ($t_w$) of 180 s are shown in Fig. 7. With increase in $\tau_p$ and $f_r$, $d_m$ increases. With the application of ultrasonic vibration, the collision probability of elements increase and the agitation of the working fluid, which results, improve discharge dispersion. Consequently, TiC generation reaction is promoted. By increasing $f_r$, the contact angle between melting TiC and the substrate decreases, and the vaporization explosion pressure also decreases. Therefore, $d_m$ increases when the ultrasonic vibration is applied to the substrate. Using XRD Al, TiC, Ti$_2$A1C and TiAl$_3$ were identified in the modified layer which is not shown here. When the ultrasonic vibration is applied, the relative intensity ratio of TiC to Al increases. The charac-
Fig. 7 The effects of ultrasonic vibration of substrate and pulse width on the modified layer thickness.

Fig. 9 Vickers microhardness profiles on the cross-sectional modified layers with and without ultrasonic vibration.

characteristic X-ray intensity profiles of EPMA on the cross-section of modified layer are shown in Fig. 8. The intensity of Ti–Kα and C–Kα are increasing close to the surface of the modified layer. On the other hand, the Al–Kα intensity increases with increasing distance from the surface. The modified layer processed with a high \( f_r \) of 94.2 kHz (Fig. 8(b)) shows definitely higher intensities of Ti–Kα and C–Kα than those in the layers without ultrasonic vibration, which is shown in Fig. 8(a). The hardness profiles of the cross-sectional modified layers are shown in Fig. 9. The maximum hardness value is obtained close to the modified layer surface in all cases, and this value gradually decreases to that of the substrate as we move inward. The hardness profile reveals a relationship with the distribution of Ti and C on the layer. The layer processed without ultrasonic vibration has the maximum hardness value of 320 HV whereas for the layer processed with ultrasonic vibration at frequencies of 28.8 and 94.2 kHz, the maximum hardness value are 390 and 410 HV respectively.

3.2 Effect of the Ultrasonic Vibration on Electrode

When the ultrasonic vibration is applied to the electrode, many convex-shaped craters are generated by single discharge on the substrate, because elements transfer from the electrode is promoted by the acceleration of ultrasonic vibrations. The effects of \( f_r \) and \( \tau_p \) on \( d_m \) are shown in Fig. 10. Just as in the case where the ultrasonic vibration is applied to the substrate, the modified layer thickness \( (d_m) \) increases with the application of ultrasonic vibration to the electrode and with the increase in \( \tau_p \). However, \( d_m \) decreases with increase in \( f_r \). The volume fraction of chemical compounds and elements by XRD in each modified layer and \( d_m \) for various conditions of ultrasonic vibration are shown in Fig. 11. Without ultrasonic vibration, though the \( d_m \) does not increase, even if the \( t_w \) increases, but the volume fraction of TiC increases. For the ultrasonic vibration of 26.1 kHz, the TiC volume fraction and \( d_m \) are larger than those for 102 kHz. The ultrasonic vibration acceleration was calculated. Assuming \( A \) is the positive am-

Fig. 8 Characteristic X-ray intensity profiles of EPMA on the cross-sectional modified layer, (a) without ultrasonic vibration, (b) with ultrasonic vibration on substrate (94.2 kHz). Process parameters: \( \tau_p = 256 \mu s, I_p = 15 \) A, \( E_g = 150 \) V, \( D_r = 0.33 \) and \( t_w = 180 \) s.

Fig. 10 The effects of ultrasonic vibration of electrode and pulse width on the modified layer thickness.

Fig. 11 The ratio of compound and element in modified layer. Process parameters: \( \tau_p = 256 \mu s, I_p = 15 \) A, \( E_g = 150 \) V and \( D_r = 0.33 \).
plitude and $f_c$ is the frequency, the displacement ($x(t)$) can be expressed as a function of time ($t$) by the following equation.

$$x(t) = A \sin(2\pi f_c t)$$

Differentiating this equation twice with respect to $t$.

$$d^2x(t)/dt^2 = 4\pi^2Af_c^2 \sin(2\pi f_c t)$$

The left-hand side term $d^2x(t)/dt^2$ represents the acceleration of the substrate or electrode surface. The maximum accelerations for each frequency are shown in Table 2. The transfer of material from the electrode to substrate is promoted for large accelerations applied to the electrode. With an ultrasonic vibration of 26.1 kHz applied to the electrode, $d_m$ is larger than that obtained for 102 kHz. The transfer of the material from the electrode to substrate is inhibited, as a large acceleration is applied to the substrate. With an ultrasonic vibration of 28.8 kHz applied on the substrate, $d_m$ is larger than that for 94.2 kHz.

### 3.3 The generating process of chemical compounds in the modified layer

The result of DTA test using a powder mixture of Ti, Al and C mixed at the mole ratio of 2:1:1 is shown in Fig. 12. This composition ratio was selected for forming TiC and TiAl in the ratio of 1:1, after these powders react perfectly. The endothermic reaction that results from the melting of Al occurs at 920 K. The exothermic reaction however occurs at about 940 K and 1040 K. TiAl$_3$ is identified in the sample, which heated to 993 K, by XRD. TiAl$_3$, TiAl and Ti$_2$AlC are also identified in the sample heated to 1040 K. There is a weak exothermic reaction at about 1600 K. TiC is newly identified in the sample heated to 1673 K, and TiAl and TiAl$_3$ are decomposed. It has been reported that TiAl$_3$ is dissolved at 1223 K, and TiC is formed at 1533 K. On one hand, heat generated by the formation reaction of TiAl$_x$ stimulates TiC formation and on the other, the heat of reaction by the generation of TiC stimulates the decomposition of TiAl$_x$. Ti, which is a constituent of TiC, reacts with different C. It is reported that Al acts as a catalyst of the TiC formation reaction. Though in actual EDA the heating is so quick, it can be assumed that EDA is nearly equal to DTA in the reaction processes, because TiC and Ti$_2$AlC are identified in the modified layer.

### 3.4 The effects of secondary elaboration and ultrasonic vibration on surface roughness, volume fraction of TiC and average thickness of modified layer

The surface roughness ($R_s$) of the modified layer with and without ultrasonic vibration previously described is about 50 μm. Secondary elaboration with small amount of heat flow using a short pulse ($\tau_p = 32$ μs) and low discharge current ($d_m = 5$ A) conditions was carried out in order to improve surface roughness. Cast Ti-36 mass%Al solid and green compact of 16 mm diameter and 2 mm thickness were used as the electrode. $R_s$ and $d_m$ after secondary elaboration are shown in Fig. 13. If the green compact electrode is used in both primary EDA and secondary elaboration, though modified layer abounds with TiC, the surface roughness is high. Whereas the TiC formation is not so abounding, the surface roughness is low, if the cast solid electrode is used in both primary EDA and secondary elaboration. When the green compact electrode is used in primary EDA and cast solid electrode is used in secondary elaboration, $R_s$ is not so different with or without ultrasonic vibration, but $d_m$ with ultrasonic vibration is thicker than that without. The secondary elaboration with a short $\tau_p$ is effective for the improvement on surface roughness.

### 4. Conclusion

A new process of electrical dischared alloying with green compact electrodes and ultrasonic vibration was carried out.

![Fig. 12](image1.png) Heat flow of differential thermal analysis using the Ti, Al and C powders at the mole ratio in 2:1:1.

![Fig. 13](image2.png) The effects of ultrasonic vibration and electrode material on the-modified layer thickness after secondary elaboration (US: ultrasonic vibration).
for surface modification of diecasting aluminum alloy. The following results were obtained:

(1) The modified layer’s main constituents are TiC, Ti$_2$AlC, TiAl$_3$ and non-reacted aluminum. The elemental distribution profiles of the constituent elements on the cross section of modified layer show a compositional gradient.

(2) Using the ultrasonic vibration on the substrate, an increase in the pulse width and ultrasonic vibration frequency results in an increase in the modified layer’s thickness. The maximum hardness of the layer processed without ultrasonic vibration is 320 HV. The hardness with ultrasonic vibration is higher and can be changed in the range of 390–410 HV by controlling the frequency.

(3) Process parameters such as frequency of ultrasonic vibration on the electrode change the modified layer thickness and TiC volume fraction.

(4) The chemical compounds formed by electrical discharge alloying on the surface are similar to those formed in differential thermal analysis using aluminum, titanium and carbon powders.

(5) The secondary elaboration using the cast solid electrode with a short pulse width and low discharge current is effective for the improvement of surface roughness of modified layer. When green compact electrode is used in primary electrical discharged alloying and the cast solid electrode is used in secondary elaboration, surface roughness is not so different for the cases with or without ultrasonic vibration. However, the thickness of the modified layer formed with ultrasonic vibration is thicker than that without.

REFERENCES