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Formation of surface layer based on Al₃Ti on aluminum by laser cladding and its compatibility with ceramics

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Abstract

Intermetallic compound Al_3Ti or intermetallic compound matrix composite (IMC) surface layers were formed on Al surface by laser cladding. To form sound IMC surface layers, laser conditions must be controlled to suppress the melting of base metal. With increasing the volume fraction of ceramics in the IMC layer, it needed higher laser power to obtain IMC layer although the control of laser conditions became easier. During laser cladding, TiB₂ melted by laser irradiation and then homogeneously precipitated as fine particles at a cooling stage. On the contrary, TiC and SiC hardly melted and were dispersed in Al_3Ti matrix. SiC reacted with Ti to form titanium-silicide or TiC, which made the composition of matrix richer in Al than Al_3Ti and caused degradation of the wear property. IMC surface layer improved the wear property of Al substrate. The particle size as well as volume fraction of dispersoid ceramics affected the wear property. (C) 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Aluminum and its alloys are light materials and now going to be used in a wider field. However, their low wear resistance prevents wider prevailing. For improvement of the wear properties, surface modification is effective. For the surface modification of Al alloys, alumite [1] treatment or spraying [2] is well known. But the surface modified layers produced by the processings have not been satisfactory in thickness or adherence to base metal, because they easily break away in case base materials have low strength and are likely to be deformed.

The authors have successfully formed intermetallic compound Al_3Ti layer on Al surface by the laser processing [3]. By irradiating laser beam to the powder mixture of Al and Ti previously placed on Al base metal, the mixture was melted and titanium aluminide alloyed layers with a thickness of 400 µm were formed on Al base metal relatively at high speed. At the same time, the binding between base metal and surface layer was ensured because of the superficial melting of base

metal. By the presence of hard intermetallic compound on Al surface, wear property was remarkably improved especially on the high speed sliding condition. The wear properties of the surface layers were strongly dependent on their structures and if Al existed in the surface compound layer due to the dilution by base metal, the wear property remarkably degraded [4]. So optimum process to form sound Al₃Ti surface layer was concluded to be a laser cladding process defined as follows.

The composition of preplaced powder mixture is Al–25 at%Ti, which is the stoichiometric composition of Al₃Ti, to give higher formability of surface layers. To avoid the dilution of surface layer by over melted base metal, the laser conditions, such as defocus distance, laser power and laser traveling speed, must be controlled to suppress the melting the base metal.

In this work, intermetallic compound Al₃Ti surface layer was formed by the optimization of laser power. Moreover, by using the mixture of Al, Ti and ceramics powders as preplaced powders, Al₃Ti based intermetallic compound matrix composite (IMC) layers [5,6] were formed to give surface layers higher wear properties. Laser irradiating condition to obtain sound layer was examined and compared with that in case of Al₃Ti layer. The dispersion state of ceramics was examined by the

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microstructural observations and the compatibility of Al_3Ti matrix with ceramics was investigated by X-ray diffraction analysis and thermodynamical analysis. Effects of ceramics dispersoids on the wear properties of obtained surface layers were estimated by Ohgoshi abrasion test and wear surface observation.

2. Experimental procedure

Fig. 1 shows the schematic view of laser cladding performed in this work. A 99.9% purity Al plate with a thickness of 6 mm was used as a base metal. To increase the laser beam absorption ratio which is extremely low for Al, blasting treatment was performed on the surface of the base metal. The powders used for laser cladding were pure Al (particle size $35 \,\mu$ m), Ti ($45 \,\mu$ m), TiB₂ ($45-150 \,\mu$ m), TiC ($20-45 \text{ or } 2-5 \,\mu$ m), SiC ($20-45 \,\mu$ m). These powders were mixed to the desired compositions and adhered as a powder bed on the base metal with ethyl silicate binder (colcoat HAS-10). Thickness of the powder beds was fixed to $400 \,\mu$ m.

Continuous CO₂ laser beam (Mitsubishi MEL 15S2, focus distance 137 mm) in multi mode was irradiated on the sample. Maximum laser power was 2.5 kW. To obtain laser clad layer with width, laser beam was upper defocused about 10 mm. As reported in the previous paper, in the case of laser cladding on Al surface, voids are likely to be included in clad layer. So beam traveling was fixed to relatively low speed, 1.67 mm/s to gain longer solidification time. To avoid oxidation of the samples or generation of plasma, helium assist gas was flown in the parallel direction of laser beam at a flow rate of $1.7 \times 10^{-4} \text{ m}^3/\text{s}$.

The structure of laser clad layer was observed by scanning electron microscope (SEM). The synthesized phases by laser irradiation were identified by energy



Fig. 1. Schematic illustration of laser cladding.

dispersive X-ray (EDX), electron probe micro analyzer (EPMA) analyses and X-ray diffraction analysis using Co K_a radiation. To monitor the changes in the melting mass of base metal, the sample was cut to the vertical direction of laser traveling and the cross section was observed.

The mechanical properties were examined by Vickers hardness measurements and Ohgoshi abrasion test using SUJ2 abraser. For abrasion test, load and sliding distance were fixed to 10 N and 100 m, respectively. Sliding speed was 1.12, 2.37 and 4.36 m/s. For the investigation of wear mechanism, wear surfaces of the IMC layers were observed by SEM. To avoid the effect of humidity or presence of moisture on the samples, samples including abrasers were kept in the vacuum chamber just before the abrasion test.

3. Results

3.1. Formation of the Al_3Ti and the Al_3Ti based IMC clad layers

To obtain clad layer well bound with Al base metal, laser power should be supplied enough to melt not only cladding powders but Al base metal superficially. Otherwise, chemical binding between base metal and surface layer is not obtained and surface layer will be broken away easily.

Table 1 shows the formability of laser clad layer when each type of powder mixtures was used as cladding materials. When the mixture of only Al and Ti powders was used as cladding material, surface layer well bound with base metal was obtained in wide laser conditions. But by adding ceramics powder, it needs higher laser power to obtain clad layer. This is because ceramic powders with low heat conductivity interrupted the heat transfer toward base metal.

Table 1

Formability of laser clad layer when each type of powder mixture was used

Starting powder	Laser power		
	1.5 kW	2.0 kW	2.5 kW
Al-25 at%Ti	0	0	0
(Al-25 at% Ti)-10 vol% TiC	Δ	0	0
(Al-25 at% Ti)-20 vol% TiC	Δ	0	0
(Al-25 at% Ti)-30 vol% TiC	Δ	0	0
(Al-25 at% Ti)-40 vol% TiC	Х	Δ	0
(Al-25 at% Ti)-10 vol% TiB ₂	0	0	0
(Al-25 at% Ti)-20 vol% TiB ₂	Δ	0	0
(Al-25 at% Ti)-30 vol% TiB ₂	Х	Δ	0
(Al-25 at %Ti)-40 vol% TiB ₂	Х	Х	Х

O, formation of clad layer well bound with substrate; Δ , the binding is unstable with the position; X, clad layer is not bound with substrate and easily broken away.

3.2. Microstructure of the clad layers

Figs. 2 and 3 show the microstructures and the X-ray diffraction patterns of Al_3Ti surface layer prepared by various laser powers. In the case of laser power of 1.5 kW, the surface layer was consisted of only Al_3Ti phase. But in case of 2.0 kW laser, the surface layer was consisted of Al (contrasted darker) as well as Al_3Ti (contrasted brighter). This Al comes from base metal due to over melting the base metal and redistributed especially near the surface. In case of 2.5 kW laser, base metal was considerably melted and consequently, the volume fraction of Al_3Ti contrasted brighter became smaller.

Fig. 4 shows the Vickers hardness profiles of obtained samples measured as a function of the distance from the surface. Hardness of Al free Al₃Ti surface layer (1.5 kW laser power) exhibited about 500 HV, which is about the same as that of bulk Al₃Ti. Up to 200 μ m distance from surface, hardness remained 500 HV and the drastically decreased down to 30 HV, hardness of base metal. But in the diluted surface layer (2.0 kW), the hardness decreased down to 100 HV especially near the surface because of Al, although hardness was 400 HV adjacent to the bondline between surface layer and substrate. To obtain sound intermetallic compound surface layer, melting of base metal must be minimized by the control of heat input.

Fig. 5 shows the microstructures of obtained IMC layers. The thickness of obtained layer is about $200 \,\mu m$.

In the Al₃Ti/TiB₂ cladding, fine particles with an average size of $2 \mu m$ were homogeneously dispersed in Al₃Ti matrix. By EDX, EPMA and X-ray diffraction analyses, these particles were confirmed to be TiB₂. As the starting TiB₂ powder is 50 µm in size, TiB₂ is considered to melt during laser irradiation and then precipitate in Al₃Ti matrix.

In the Al_3Ti/TiC cladding, particles about 30 µm in size were dispersed in Al_3Ti matrix. These particles were confirmed to be TiC. As the morphology is hardly changed from that of starting powders, TiC does not melt during laser cladding and was dispersed homogeneously. Partially fine Ti₂AlC particles were observed around TiC particles near the surface.

For the Al₃Ti/SiC layer, SiC particles were dispersed in matrix in the original morphology. However, formation of reaction layer (presumably Ti_5Si_3) was confirmed on the SiC/matrix interface. In the matrix adjacent to the SiC particles, moreover, fine TiC particles were observed. Due to the reaction with SiC particles, the matrix changed the composition richer in Al and the structure became the dual phase structure consisting of Al (contrasted darker) as well as Al₃Ti.

Consequently, hardness of the matrix decreased to 100 HV in Al₃Ti/SiC layer, although hardness remained 500 HV in Al₃Ti/TiB₂ or /TiC clad layer.

3.3. Wear properties

Fig. 6 shows the wear resistance of Al base metal, $Al_3Ti + Al$ and Al_3Ti surface layers formed by laser



Fig. 3. X-ray diffraction patterns of the surface layer formed by the laser power of (a) 1.5, (b) 2.0, and (c) 2.5 kW.



Fig. 2. Microstructures of surface layer prepared at laser power of (a) 1.5, (b) 2.0, and (c) 2.5k W.

cladding at a laser power of 1.5 and 2.0 kW, respectively. From this figure, it is confirmed that Al was improved in the wear property by laser cladding. There are large differences in wear properties between Al₃Ti and Al₃Ti + Al layers. Even the small volume fraction of soft Al causes the degradation of the wear properties.

Fig. 7 shows the changes in wear resistance of laser clad layers as a function of volume fraction of ceramics. Al₃Ti/ceramics clad layer showed superior wear property to Al₃Ti clad layer. This is due to the existence of ceramics with larger hardness and higher melting temperature. With increasing the volume fraction of ceramics up to 30 vol%, clad layer revealed superior wear property. But when the volume fraction of ceramics exceeded 30 vol%, wear property hardly changed. In comparison with Al₃Ti/TiB₂ clad layer, Al₃Ti/TiC clad layer had a better wear property, although there are no significant differences between TiC and TiB₂ in the melting temperature or the hardness.



Fig. 4. Vickers hardness profiles of sound Al_3Ti and diluted $Al_3Ti + Al$ layers as a function of the distance from the surface.

4. Discussion

To obtain sound clad layer, melting of base metal must be minimized by the control of heat input.

Fig. 8 shows area variation of melted substrate as a function of laser power in case of Al_3Ti , $Al_3Ti-10 vol\%TiB_2$, $Al_3Ti-10 vol\%TiC$ cladding. Although mass of the melted Al is very sensitive to the heat input in the Al_3Ti cladding, it hardly changed in the case of IMC cladding. So it can be concluded that application of laser which can precisely control the heat input is effective for the surface modification of Al. In comparison with Al_3Ti cladding and it can be recognized from this figure, too, that higher laser power is necessary to obtain IMC surface layers. This is because, by adding ceramics with larger specific heat or latent heat, heat input by laser is more consumed to heat or melt powder bed and then smaller heat is transferred to base metal.

 TiB_2 , TiC, SiC ceramics particle reinforced IMC layers were formed by laser irradiation. TiB_2 particle was recognized to melt during laser irradiation and then



Fig. 6. Area variation of melted substrate as a function of laser power in case of Al₃Ti, Al₃Ti-10 vol%TiB₂, Al₃Ti-10 vol%TiC cladding.



Fig. 5. Microstructures of obtained (a) Al₃Ti/TiB₂, (b) Al₃Ti/TiC and (c) Al₃Ti/SiC layers.

precipitate in Al₃Ti matrix. However, there is no difference among ceramics used in this work, and the melting point of TiB₂ is about 3000 K to which temperature clad layer is not heated by laser irradiation. It is reported the liquidus temperature decreases down to about 950 K in the Al rich composition range [7]. After peritectic reaction, Al₃Ti and TiB₂ coexist in the equilibrium state [8]. On the contrary, for Al–TiC or –SiC system, many compounds with higher melting temperature such as Ti₂AlC exist and the liquidus temperature is relatively high [9]. This is why only TiB₂ was considered to melt during laser cladding.

For the reactivity of each ceramic with matrix Al₃Ti, SiC considerably reacted most and TiC slightly reacted.

In ternary Ti–Si–C phase diagram, in the Ti rich composition, there is a wide composition range where Ti, TiC and Ti₅Si₃ phases coexist. This fairly corresponds



Fig. 7. Wear resistance of Al₃Ti, Al₃Ti + Al layers and Al substrate.



Fig. 8. Changes in the wear resistance of IMC layers as a function of volume fraction of ceramics.

well with the results obtained by structural observation. In SiC fiber reinforced Ti MMC alloys, it is reported Ti_5Si_3 layer was formed on the interface between SiC and matrix [10]. Ti_5Si_3 has the biggest negative heat of formation among titanium silicides [11], which may be related to this preferred formation of Ti_5Si_3 phases.

Fig. 9 shows the changes in the ΔG for the carbide formation as a function of the temperature calculated from thermodynamical data [12]. As is evident from this figure, affinity of C with Ti is much larger than that with Si or Al. The heat of formation for Al–Ti and Si–Ti is 28 and 45 kcal mol [13], respectively, showing that the affinity of Ti with Si is larger than that with Al. So when the mixture of Al, Ti and SiC are laser melted, the following reaction can be thermodynamically proposed to occur.

 $8Ti + 3SiC - Ti_5Si_3 + 3TiC$

To strengthen the binding between ceramics and matrix, the reaction between them is preferable. However, such ceramics as SiC that reacts mainly with Ti are not preferable because the composition of matrix became richer in Al than the stoichiometric composition of Al_3Ti and the structure became dual phase consisting of soft Al as well as Al_3Ti .

In the wear properties of laser clad IMC layers, Al_3Ti/TiC clad layer had a better wear property than Al_3Ti/TiB_2 clad layer. There are no significant differences between TiC and TiB₂ in the melting temperature or the hardness, which affects the wear property,



Fig. 9. Free energy changes for the carbide formation reactions.



Fig. 10. Wear surfaces of (a) Al₃Ti, (b) Al₃Ti/TiC, (c) Al₃Ti/TiB₂ and (d) Al₃Ti/fine TiC IMC layers.

between TiC and TiB_2 . To investigate this difference in wear property, the wear surface was observed.

Fig. 10 shows the wear surfaces of Al₃Ti, Al₃Ti/TiC and Al₃Ti/TiB₂ clad layers. Matrix Al₃Ti of composite clad layer exhibited similar wear surface to Al₃Ti clad layer. It is noticed that there were no special wear surfaces in fine TiB_2 particle although wear trace could be obviously observed on the coarse TiC particle. In the previous paper, it was confirmed that not sound Al₃Ti clad layer diluted by Al was much inferior in wear property to sound Al₃Ti clad layer because of the existence of soft Al. As well, TiB₂ particle is fine, so the effect of matrix can not be neglected. Moreover, when particle size is large, matrix is preferentially worn and wear surface will not be flat. This means wear mechanism will be dominated by the wear between ceramics and abraser. As the evidence, IMC layer with fine TiC (particle size of 2 µm) exhibited almost the same wear property and wear surface [Fig. 10(d)] as that of Al₃Ti/ TiB₂ clad layer.

It is concluded that the particle size as well as volume fraction of dispersoid have an effect on the wear property. Refinement of ceramic particle size decreases the wear property while it is effective to improve hardness or mechanical properties.

5. Conclusion

Al₃Ti intermetallic compound and Al₃Ti–ceramic composite (IMC) layers were elaborated on aluminum surface by laser cladding. Obtained results were as follows.

- To obtain sound surface alloyed layer adherent to base metal and free from dilution of Al, heat input had to be precisely controlled to minimize the melting of base metal. With increasing the volume fraction of ceramics in the clad layer, it needs higher heat input to obtain sound surface layer. The volume of melted substrate, however, changed less with laser power in comparison with Al₃Ti cladding. As the result, the control of laser power became less precise in the cladding of IMC layers.
- 2. In the Al₃Ti/TiB₂ cladding, TiB₂ melted during laser cladding and then homogeneously precipitated to fine particles with an average size of 2 μm. TiC particle hardly melted by laser irradiation and is dispersed in Al₃Ti matrix. SiC hardly melted during laser irradiation, but reacted with Ti in molten Al–Ti matrix to form titanium–silicide or TiC. As the result, matrix became richer in Al

than Al₃Ti and dual phase structure consisting of Al as well as Al₃Ti. These compatibilities of Al₃Ti with ceramics were interpreted thermodynamically.

3. Surface clad Al₃Ti layer showed the same hardness as that of the as cast Al₃Ti and improved the wear properties of Al base metal. By addition of ceramics to Al₃Ti, wear property was improved more. Particle size as well as volume fraction of the dispersoid ceramics had an effect on the wear property of clad layer. Refinement of ceramic particle size decreased the wear property.

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