



C–O bond enhancing direct bonding strength between plastic and pure titanium



Katsuyoshi Kondoh*, Junko Umeda

Joining and Welding Research Institute, Osaka University, 11-1 Mihogaoka, Ibaragi, Osaka 567-0047, Japan

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ABSTRACT

Direct bonding process by using the conventional hot pressing was applied to prepare the dissimilar materials consisting of the thermoplastic resin and pure titanium (Ti) material. In employing the pressing temperature at the melting point of plastics, the interfacial bonding shear strength of the dissimilar material using polyamide66 (PA66) was drastically increased. Microstructure and phase analysis clarified that C=O double bonds of the carbonyl group was thermally decomposed and oxygen atoms contributed to diffusion into pure Ti or oxides formation at the interface. In addition, the chemical reaction of C–H and N–Ti formation was also effective to the interfacial bonding improvement. On the other hand, when polystyrene (PS) with no functional group including C–O/C=O bond was employed, for example, the PS–Ti dissimilar material showed no bonding strength even then the bonding temperature was close to 300 °C.

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1. Introduction

Carbon fiber reinforced plastic (CFRP) is widely employed as engineering materials in the transportation industry such as airplanes, automobiles, high-speed trains and marines because of its low density, outstanding corrosion resistance, high specific strength and Young's modulus compared to the conventional industrial metals such as steels and aluminum alloys [1]. In particular, CFRP material, using thermoplastic resins as a matrix, possibly reduces the processing cost due to its excellent formability in pressing and recyclability [2]. From high reliability and enhanced safety points of view, however, the hybrid materials design using both CFRP and metals called as “multi-materials design” is necessary for further lightweight of the components in the transportation industries. In joining the metal sheets and CFRP flat panels, the use of adhesive agents [3,4] or mechanical joints and fastening by bolts or rivets [5,6] is common in the industries because of their ease of assembly. They are, however, not complete in joining due to its insufficient reliability and weight increment of the components. To establish a direct bonding process between CFRP and industrial metals, the fundamental researches using ultrasonic welding [7,8], friction welding [9] and laser welding [10,11] are recently carried out, and successfully achieved a high bonding strength between metal sheets and CFRP or thermoplastic materials by each process.

Regarding the bonding mechanism in each process, for example, Fourier-transform infrared spectroscopy (FTIR) analysis on the bonding interface indicated that a physicochemical interaction based on hydrogen bonds originated in the polyamide caused a chemical bonding of the plastic to aluminum materials [11]. In addition, a high gas pressure in gas bubbles generated from the molten plastic material assisted to directly bond the plastic to the metal surface, and resulted in formation of thin oxide layers at the interface [10]. In use of friction welding, the similar mechanism in using laser welding mentioned above was reported [9]. On the other hand, the mechanical interlocking effect at the interface was also necessary for a strong bonding strength in each process [7,9,11]. The dissimilar bonded materials between CFRP or plastic and common metals prepared by the above processes showed an enough bonding stress, and the fractures occurred on the plastic side, not at the bonding interface. The bonding mechanism, however, has not been completely clarified in these studies. In particular, the detail analysis at the local area near the interface is not enough to understand the chemical reaction between the plastic and metals by considering the molecular structural changes of plastic materials at elevated temperature in bonding. This study investigates the effect of C=O double bond of the carbonyl group in polyamide66 on the direct bonding behavior between the plastic and pure titanium plate by using FTIR, Transmission Electron Microscope with Energy dispersive X-ray spectrometry (TEM-EDS) and X-ray Photoelectron Spectroscopy (XPS), and establishes a chemical bonding model for the dissimilar materials.

* Corresponding author.

E-mail address: kondoh@jwri.osaka-u.ac.jp (K. Kondoh).

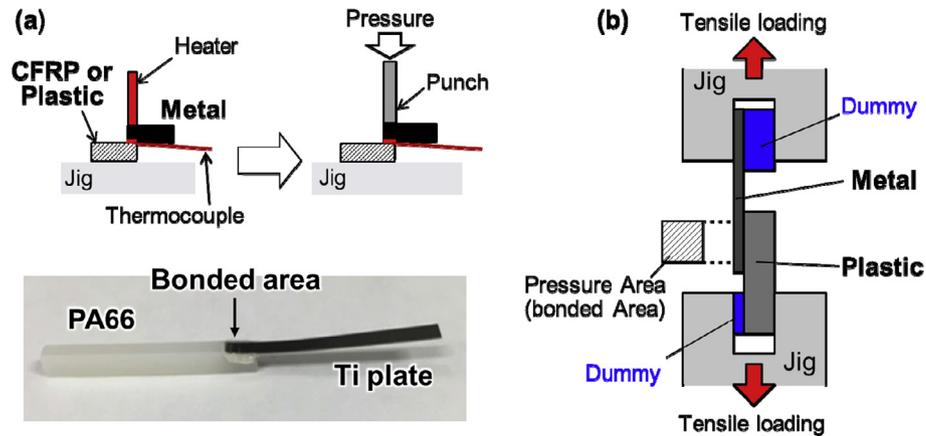


Fig. 1. Schematic illustration of direct bonding process between CFRP or plastic and metal plate (a) and shear bonding strength test using 50 kN hydraulic tensile test machine (b). In (a), pure Ti material employed as a metal plate.

2. Experimental procedure

Pure Ti plate with a purity of 99.5% was employed in this study. It had a mirror-finished surface through various polishing treatments using fine alumina particles (mean diameter; 50 nm) and diamond lapping paste compounds (mean diameter; 0.25 μm). The plates of polyamide66 (PA66), polystyrene (PS) and polyethylene terephthalate (PET) were also used for bonding test after polishing treatment using #4000 abrasive paper. The melting point of each plastic was measured by differential thermogravimetric analysis (DTA). The direct bonding process of each plastic to metal plate is schematically illustrated in Fig. 1 (a). The metal plate was heated by contact with a small soldering iron device, and its heat conduction effectively caused a temperature increase of the plastic. The temperature profile at the interface between them was measured by a thermocouple inserted in the interface. When the interfacial temperature reaches the target, the thermocouple is pulled out, and immediately 5 MPa pressure is applied to pure Ti by an upper punch (4 mm \times 4 mm) for 8 s. Examples of the directly bonded material of PA66 to pure Ti plate is also shown in Fig. 1 (a). TEM-EDS was applied to analyze oxygen atoms behavior at the bonding

interface, and FTIR and XPS analysis was carried out to investigate the molecular structural changes of the plastic materials before and after bonding to the Ti plate. A shear bonding strength of the dissimilar material was measured as illustrated in Fig. 1 (b).

3. Results and discussion

Fig. 2 shows a dependence of shear bonding strength of the dissimilar bonded materials on the interfacial temperature, where the melting point of PA66, PET and glass transition temperature of PS measured by DTA are 248 $^{\circ}\text{C}$, 242 $^{\circ}\text{C}$ and 98 $^{\circ}\text{C}$, respectively. They are close to the data measured in the previous studies [12,13]. Pure Ti plate was used as a counter material. In case of the plastic contains a carbonyl group including C=O double bond such as PA66 and PET, their shear bonding strength of both dissimilar materials (Ti-PA66 and Ti-PET) drastically increases when the interfacial temperature is over the melting point of each plastic material. The average of the bonding strength in Ti-PET dissimilar material is a little higher than that of Ti-PA66 bonded material. In addition, the bonded materials easily separate and their shear strength is zero in employing the interfacial temperature in bonding less than

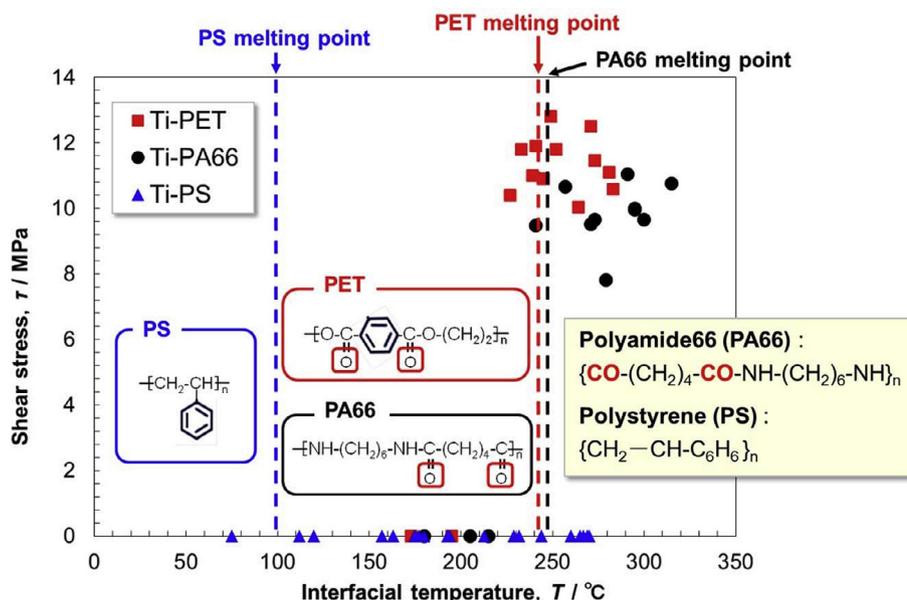


Fig. 2. Shear bonding strength of dissimilar materials between pure Ti plate and PA66, PS and PET plastic materials prepared by changing bonding temperature.

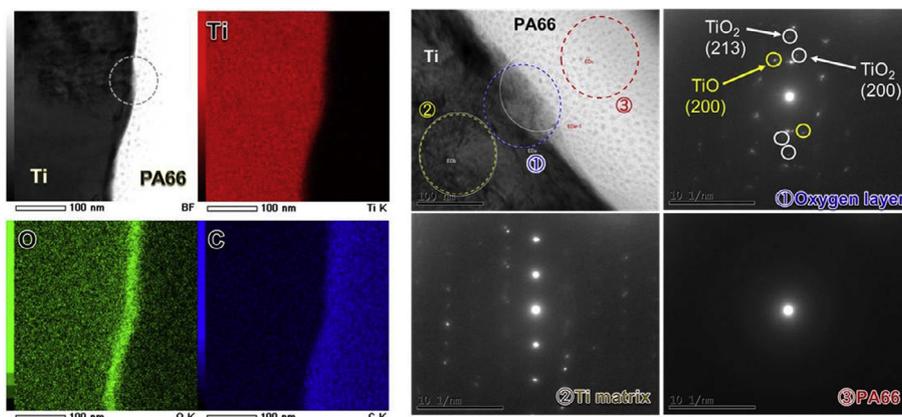


Fig. 3. TEM-EDS and electron diffraction analysis on bonding interface of Ti-PA66 bonded material.

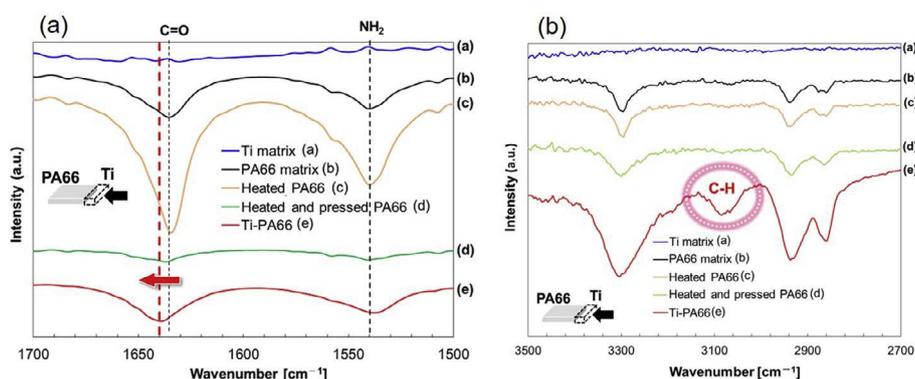


Fig. 4. IR spectra of raw pure Ti plate (a), as-received PA66 material (b), PA66 after heat treatment (HT) at 260 °C (c), PA66 after HT at 260 °C under 5 MPa pressure (d), and PA66 of the bonded material (e).

each melting point. On the other hand, Ti-PS dissimilar bonded materials have no bonding and joining behavior even the interfacial temperature is over its melting point of 98 °C. It is concluded that the carbonyl group with C=O double bond are necessary to directly bond the plastic to pure Ti and the bonding temperature must be controlled over the melting point of the plastic material.

TEM-EDS analysis in Fig. 3 indicated oxygen concentration area at the interface of the Ti-PA66 bonded material, and its electron diffraction detects some oxides (TiO₂ and TiO) formation in the layer. By considering an interstitial solubility of oxygen in α -Ti is 33% in Ti-O binary phase diagram [14], the oxides formation suggests many oxygen atoms diffused from PA66 into pure Ti through the bonding interface during hot pressing.

As shown in Fig. 2, the shear bonding strength test already indicated C=O bond has an important role on the direct bonding of PA66 to Ti plate. First of all, FTIR analysis was conducted to detect C=O spectrum changes in bonding as shown in Fig. 4. As mentioned above, the conventional hot pressing process was applied in the preparation of Ti-PA66 dissimilar bonded material. That is, the effects of the thermal factor and pressure in hot pressing on the chemical reaction at the interface should be considered. Therefore, as-received PA66 material, PA66 after heat treatment (HT) at 260 °C, PA66 after HT at 260 °C under 5 MPa pressure, and PA66 separated from the bonded material were prepared for FTIR analysis. Each spectrum at wavenumbers 3300 cm⁻¹, 3100 cm⁻¹, 1633 cm⁻¹, 1539 cm⁻¹ is amino group (NH₂, stretch), aromatic C-H group (stretch), C=O bond and NH₂ (bending), respectively [15,16]. The specimens (c) and (d) show no change in C=O spectrum compared to the original PA66 (b), that is, the molecular

structural change of C=O bond never occurs by pressure and high temperature over its melting point. The specimen (e), however, obviously reveals a significant variation of C=O double bond. The PA66 specimen separated from the dissimilar bonded material shows an increment of wavenumber (κ) compared to the reference specimen (b). That is, it is obvious that the direct bonding behavior between PA66 and pure Ti by hot pressing causes molecular structural changes of PA66 material. A wavenumber, κ is expressed as a modified Hooke's Law in the below by considering the bond as a spring.

$$\begin{aligned} \kappa &= f/c = 1/(2\pi c)\sqrt{k/\mu}, \quad \mu(\text{reduced mass of atoms}) \\ &= m_1 m_2 / (m_1 + m_2) \end{aligned} \quad (1)$$

where k ; spring constant for the bond, m ; mass of atom, f ; frequency and c ; velocity of light ($=3 \times 10^{10}$ cm/s).

When the bonding strength between two atoms (m_1 and m_2) increases, the increment of a spring constant occurs, and results in the increase of a wavenumber (κ value). The commercial PA66 contains two kinds of amides; X-C(=O)-Y and X-C(-O)-Y, and has a resonance structure with both amides [17]. In general the bonding strength of C=O bond is much larger than that of the latter with a covalent bond. As shown in Fig. 4, the wavenumber increment in the PA66 of Ti-PA66 bonded material means the number of X-C(=O)-Y relatively becomes much large compared to X-C(-O)-Y amide. It means C=O double bonds in the functional group (carbonyl group) are dominant in the PA66 specimen bonded to pure Ti plate. When a polarity change occurs by the electronegativity due to the bonding of another atom to X or Y atom linked up

with C atom in the functional group, the number ratio of C=O relatively increases [17,18]. In considering TEM observation result in Fig. 3, Ti atoms would chemically bond to C atoms to form metal complex during hot pressing, and resulted in C=O spectrum variation near the interface of the bonded material as shown above.

4. Conclusions

In summary, the role of C–O/C=O bonds contained in the plastic materials on the direct bonding behavior of the plastic to pure Ti, which was one of the industrial light metals by using hot pressing was investigated. Dissimilar bonded materials between pure Ti and PA66 or PET, having C=O double bonds, showed high shear bonding strength while Ti-PS bonded one had no bonding behavior. C=O bond in the carbonyl group is essential for chemical bonding between plastic and pure Ti by hot press. The oxygen atoms thermally separated from C=O bond diffused into Ti specimen, and resulted in the oxides formation at the bonding interface.

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