Title	Interfacial Structure Analysis on Direct Bonding Metals to Plastics
Author(s)	Imai, Hisashi; Kondoh, Katsuyoshi; Izawa, Takeru et al.
Citation	Transactions of JWRI. 2015, 44(1), p. 23-26
Version Type	VoR
URL	https://doi.org/10.18910/57263
rights	
Note	

Interfacial Structure Analysis on Direct Bonding Metals to Plastics[†]

IMAI Hisashi **, KONDOH Katsuyoshi *, IZAWA Takeru * and UMEDA Junko ****

Abstract

This research investigated the direct bonding mechanism of dissimilar materials such as metals and plastic by the conventional hot pressing process. The press area of 4 x 4 mm^2 was used for direct bonding. The results of the study showed that titanium was completely bonded to polyamide 66. On the other hand, titanium was not bonded to polystyrene. In the case of bonding material of titanium with polyamide 66, and oxide layer of about 20 nm as reaction layer was confirmed on the bonding interface by transmission electron microscope observation. It was considered that the origin of this oxide layer was due to oxygen constituting amide groups with C=O double bond in the polyamide 66.

KEY WORDS: (Direct bonding), (Dissimilar materials), (Amide group), (C=O double bond)

1. Introduction

Direct bonding of dissimilar materials such as metal and plastic is necessary for industry because of multi-function product manufacturing. For example, carbon fiber reinforced plastic (CFRP) is expected to be widely used for energy saving and CO_2 emission reduction in transportation industries because CFRP has excellent characteristics of lightweight, high specific strength, high corrosion resistance (1). It is necessary to bond the metals to CFRP directly to fabricate lightweight composite products. In the case of the automotive industry, mechanical fastening or an adhesive are used for joining CFRP and metal. However, there is some problem in their joining method. The adhesive VOC (Volatile Organic Compounds) regulation has been decided for adhesion methods (2). The adhesion time is too long. There is also a problem with cutting powder generation in the mechanical fastening. For such problems, the direct bonding of the CFRP and metal has been investigated. Laser-Assisted Metal and Plastic Joining Method (LAMP) can directly bond metal with CFRP(3,4). Some investigations were carried out using the ultrasonic metal welding technique for joining sheet aluminum to CFRP (5). However, the bonding mechanism is still largely unknown. In our research groups, CFRP and metal could be bonded directly by the conventional hot pressing process. Carbon fiber and graphite were generally never bonded to metal sheets by this process. Our previous research also showed that the properties of polyamide 66 as matrix of CFRP were effective for direct bonding metal to CFRP (6). In this study, the direct bonding mechanism of the metals and plastics dissimilar materials was investigated. Specifically, from a viewpoint of amide groups with C=O double bond effects, the bonding possibility of titanium and plastics (polyamide 66 and polystyrene) was examined. Interfacial structure of the bonding material was analyzed for investigation of chemical bonding by transmission electron microscope.

2. Experimental

Polyamide 66 (PA66) and polystyrene (PS) sheets were prepared for investigating direct bonding ability with metals. Polyamide 66 is used as a matrix material of CFRP, as it contains amide groups with C=O double bond. The melting point of the polyamide 66 is about 240 ℃. The melting point of the polystyrene is equivalent to the melting point of polyamide 66. On the other hand, polystyrene does not contain amide groups. Typical structural formulas of the plastics are shown in Figure 2. Pure titanium (Purity 99.5%) was used as counter materials. The surface of the metal sheet was mirror-finished with less surface roughness than 0.05μm to remove the anchor effect.

Figure 1 showed the basic principle of hot press bonding. The metal and plastic were preheated by spot heater. To measure the interfacial temperature, a K-type thermocouple was inserted into the bonding interface between the titanium sheet and plastic sheet. The preheated material was immediately pressed at 5 MPa for 8 sec. The pressed area was 4 x 4 mm^2. The shear tensile

---

† Received on July 31, 2015

* Professor
** Lecturer
*** Student

Transactions of JWRI is published by Joining and Welding Research Institute, Osaka University, Ibaraki, Osaka 567-0047, Japan

force of the bonding materials was evaluated using a tensile testing machine (AUTOGRAPH AG-X: SHIMADZU) with a test speed of 0.3 mm/min. The sample of titanium deposited on polyamide 66 was also prepared to confirm the reaction behavior at the interface (Deposited material). The interface of the test sample was analyzed by TEM-EDS.

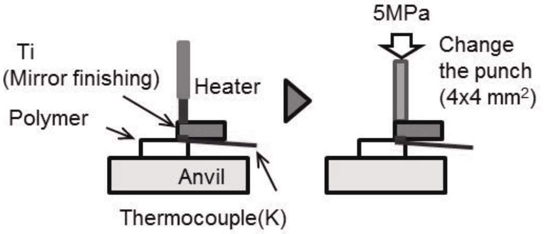
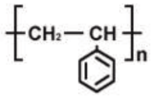


Figure 1 Basic principle of hot press bonding.

$$\left[NH(CH_2)_6NH-CO(CH_2)_4CO \right]_n$$

(a) Polyamide 66



(b) Polystyrene

Figure 2 Typical structural formulas of plastics

3. Results

Figure 3 shows shear tensile force dependence on the interfacial temperature of Ti-polyamide 66, and Ti-polystyrene bonding materials. Ti-polyamide 66 was bonded. It obviously indicated that the shear stress in case of polyamide 66 drastically increased when the interfacial temperature was over 513 K, which was the melting point of polyamide 66. On the other hand, Ti-polystyrene did not have high shear stress although the bonding interface temperature exceeded the melting point.

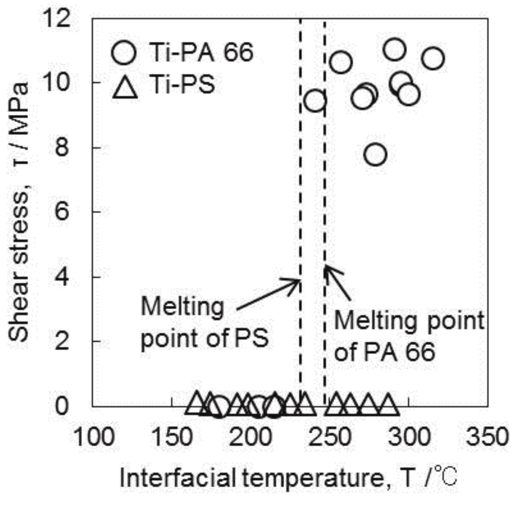
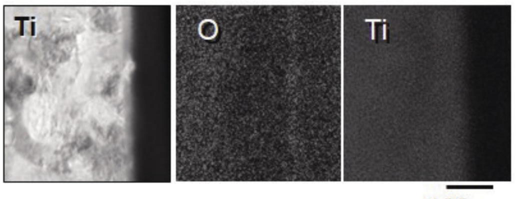
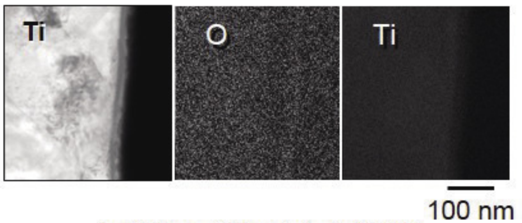


Figure 3 Dependence of shear tensile stress on interfacial temperature of bonding materials.

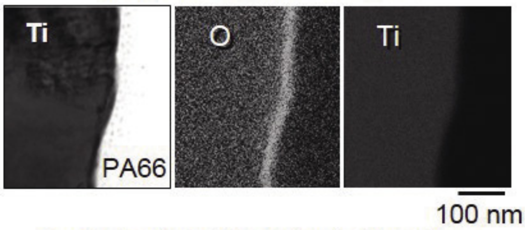
In general, the plastic enters into the surface irregularities of the metal by plastic flow at high temperature due to its low viscosity. The plastic flow becomes the anchor effect, as a result both material are joined. In this study, there was no anchoring effect in this mirror surface from the results of mechanical properties of Ti-polystyrene. Interfacial chemical reaction was also effective in bondability of metal-polymer bonding materials in this study.



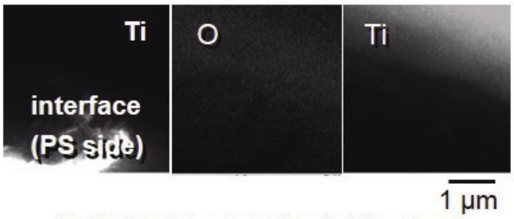
(a-1) As received Ti



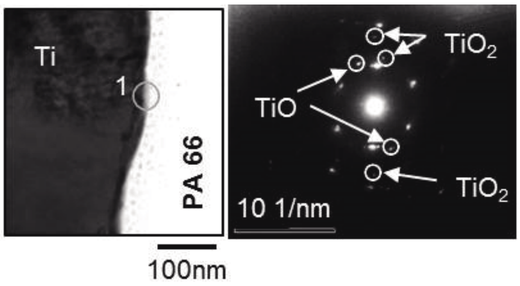
(a-2) Pure Ti heated at 513 K



(a-3) Ti-polyamide 66 bonded interface



(a-4) Ti-polystyrene bonded interface



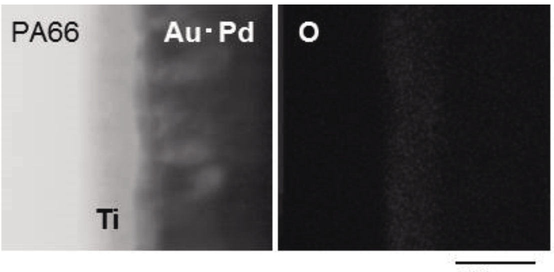
(b) Diffraction pattern of position 1 at bonding interface of Ti-polyamide 66

Figure 4 TEM-EDS analysis result (a) and diffraction pattern of bonding interface of each specimen.

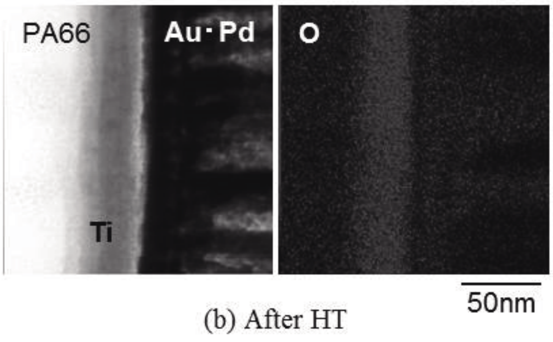
TEM-EDS analysis results and diffraction pattern of the bonding interface are shown in Figure 4. The TEM observation on received titanium and heat treated titanium at 240 ℃ are also shown in this figure. In the case of Ti-polyamide 66, oxygen concentrated layer with 20-50 nm in thickness was obviously observed at the bonding interface. This oxygen layer was thicker than the natural oxide film. TiO and TiO_2 were detected on this layer by diffraction pattern images (b). On the other hand, there was no oxygen layer at bonding interface of Ti-polystyrene.

Figure 5 showed TEM-EDS observation on the interface between deposited titanium and polyamide 66 to investigate the diffusion behavior of oxygen. The polyamide deposited with titanium was heat treated at 513 K for 1 sec in Ar gas atmosphere. The oxygen concentration at the interface remarkably increased after heat treatment. From the results of EDS point analysis, oxygen content at the interface before and after heat treatment were 25.1at% and 50.1at%, respectively. It was considered that the chemical bonding occurred by the diffusion of oxygen originated in polyamide 66 into its titanium side through the bonding interface.

The mechanism of direct bonding metal to plastics was considered as follows: The oxygen double bonds of the amide groups were separated, and oxygen atoms diffused into the titanium when the bonding interface temperature reached the melting point of the polyamide 66. At the same time, C=Ti bond was generated by the part of the double bond. It was considered to have enough bonding strength in this chemical bonding as shown the previous studies (7-11).



(a) Before HT



(b) After HT

Figure 5 TEM-EDS mapping analysis on oxygen at the interface of deposited material.

4. Conclusion

This research investigated the direct bonding mechanism of dissimilar materials as titanium and plastics by a hot press process. Titanium was completely bonding to polyamide 66 contained with amide groups. The shear stress of Ti-polyamide 66 drastically increased when the interfacial temperature was over 513 K, which was the melting point of polyamide 66. On the other hand, Ti-polystyrene did not have high shear stress although the bonding interface temperature exceeded the melting point of polystyrene. In case of Ti-polyamide 66, an oxide layer with about 20 nm as a reaction layer was confirmed on the bonding interface by TEM observation. The oxygen double bonds of the amide groups with C=O double bonds in polyamide 66 were separated and diffused into the titanium during melting polyamide 66. At the same time, C=Ti bond was generated by the part of the double bond. This chemical reaction was considered one of the mechanisms of direct bonding metal to plastics.

Acknowledgement

The authors sincerely thank the researchers of the Joining and Welding Research Institute (JWRI), Osaka University as well as T. Murakami for assistance in carrying out its TEM observation.

References

1） C. Soutis: Carbon fiber reinforced plastics in aircraft construction, Materials Science and Engineering A, 412,171–176 (2005)

2） Faisal I. Khan, Aloke Kr. Ghoshal: Removal of Volatile Organic Compounds from polluted air, Journal of Loss Prevention in the Process Industries, 13, 527–545 (2000).

3） K.W.Jung, Y.Kawahito, S. Katayama: Laser direct joining of carbon fibre reinforced plastic to stainless steel, Science and Technology of Welding and Joining, 16-8, 676-680 (2011).

4） Seiji Katayama, Yousuke Kawahito,: Laser direct joining of metal and plastic, Scripta Materialia, 59, 1247-1250 (2008).

5） Guntram Wagner, Frank Balle, Dietmar Eifler: Ultrasonic Metal Welding of Aluminium Sheets to Carbon Fibre Reinforced Thermoplastic Composites, JOM, 64-3, 401-406 (2012).

6） H. Imai, T. Izawa, K. Kondoh, J. Umeda: Direct bonding mechanism of metals with CFRP, The 5th International Symposium on Advanced Materials Development and Integration of Novel Structured Metallic and Inorganic Materials (AMDI-5) Conjunction with 6th IBB Frontier Symposium, 89 (2015)

7） P. S. Ho, P. O. Hahn, J. W. Bartha, G. W. Rubloff, F. K. LeGoues, and B. D. Silverman: Chemical bonding and reaction at metal/polymer interfaces, Journal of Vacuum Science & Technology A, 3, 739-745 (1985).

8） James M. Burkstrand: Metal‐polymer interfaces:

Adhesion and x-ray photoemission studies, Journal of Applied Physics, 52, 4795-4800 (1981).

9) P. K. Wu, T.-M. Lu: Metal/polymer adhesion enhancement by reactive ion assisted interface bonding and mixing, Applied Physics Letters, 71, 2710-2712 (1997).

10) Chang-Sheng Liang, Zhong-Fei Lv, Yang Bo, Jia-Yang Cui, Shi-Ai Xu: Effect of modified polypropylene on the interfacial bonding of polymer-aluminum laminated films, Materials and Design, doi.org/10.1016/j.matdes.2015.05.021.

11) Robert B. Grubbs: Hybrid metal–polymer composites from functional block copolymers, Journal of Polymer Science Part A: Polymer Chemistry, 43-19, 4323–4336 (2005).