報告番号	甲　第 13315 号

主 論 文 の 要 旨

論文題目　**Development of direct joining process of metals and polymers via additively fabricated anchor layer by laser induced in-situ reaction**
(レーザ誘起その場反応型付加製造によるアンカー層を介した金属/ポリマー直接接合プロセス開発)

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論 文 内 容 の 要 旨

An anchor effect, which is also called as a mechanical interlocking, is one of the joining mechanisms for metals and polymers. The anchor effect acts when polymer interlocks with asperities (i.e. dimples, grooves, pores, and protrusions) formed on metal surface. To utilize the anchor effect for joining Al alloy and polymer substrates, a novel method to fabricate an anchor layer on metal surface was introduced in the present thesis.

In Chapter 1, motivations of this research were introduced. Social backgrounds for a necessity of multi-material structure were reviewed. The multi-material structure, which is composed of high tensile strength steel, light metals, and polymers, has been adopted to an automobile body to decrease the vehicle body weight. Technologies for joining metals and polymers are important for the practical application on the multi-material structure since the use of polymer materials remarkably reduces the weight of vehicle bodies. The anchor effect is a critical factor for the direct joining between metals and polymers. The morphology of the asperities on the metal surface is responsible for changing in the metal/polymer joint strength. Conventional processes for forming the asperities on the metal surface can be roughly categorized into laser texturing, chemical etching, and sand blasting processes. These processes fabricate pores or grooves (intrusive asperities) on the metal surface by removing material. When the intrusive asperities are used, a high pressure needs to be applied during joining processes to penetrate the polymer into the asperities. Low joint strength is another representative disadvantage of metal/polymer hybrid structure. To overcome these disadvantages, an anchor layer was additively fabricated on the Al alloy substrate by laser induced in-situ reaction of Al-Ti-C powder blends bedded on the Al substrate. The goal of this study is to investigate the effects of the anchor layer forming conditions on the morphology of the anchor layer for a high joint strength. In addition, optimal joining process conditions for manufacturing directly joined Al/polymer hybrid structures were explored.

In Chapter 2, the effect of Al surface conditions on the wettability with water and epoxy resin was investigated. The metal surface condition was modified by ethanol wiping, sand-papering, and atmospheric plasma treatment. Sessile drop method was used to evaluate the wettability between the Al substrate and liquids. It was found that the wettability was influenced by organic impurities and roughness of the Al surface. The wettability greatly improved when the atmospheric plasma treatment was carried out. By the plasma treatment, the organic impurities on the as received Al substrate were remarkably removed, and Al oxide was formed on the surface of Al substrate.

In Chapter 3, the process for additively fabricating the anchor layer on an Al alloy substrate (A5052) was proposed. The anchor layer was fabricated by a single laser scanning on powder blends bedded on the Al substrate. For the powder blends, Al-Ti and Al-Ti-C powder blends were tried to induce Al-Ti and Ti-C reactions. An Al powder was also used for comparison. In the case of the Al powder, the anchor layer consisted of granular protrusions with 200 ~ 600 μm size was formed. When Al-Ti powder blend was used, a dense convex layer was fabricated on the laser irradiated region. When the Al-Ti-C powder blend was used, the anchor layer consisted of homogeneously distributed granular protrusions with < 400 μm size was formed. In addition, Al_3Ti and TiC phases were formed inside the granular protrusions and around the interface between the granular protrusions and Al substrate. It was found that the TiC phase contributed the formation of the granular protrusions since the TiC phase formed a skeleton structure of the granular protrusions. The shear strength of the Al/Polyamid-6 (PA6) joint via the Al-Ti-C anchor layer were excellent. The granular protrusions reinforced with the Al_3Ti and TiC phases formed around the interface between the granular protrusions and Al substrate allowed the anchor layer to endure high external force. In addition, many granular protrusions provided sufficient interlocking sites for PA6, resulting in the high joint strength.

In Chapter 4, optimal joining process conditions for manufacturing the Al/PA6 joints using a hot-pressing machine were explored. Semi-crystalline thermoplastics are frequently used as joining materials since the thermoplastics melt at high temperature. The mechanical characteristics of the semi-crystalline polymers are greatly influenced by crystalline characteristics of the polymer, which are determined by thermal conditions for the polymer processing. The Al alloy substrate (A5052) with the anchor layer was put on the hot plate heated to 215 °C with a PA6 substrate. The substrates were pressured for 60 s to interlock the PA6 with the anchor layer. The substrates were cooled in the hot-pressing machine (slow cooling) to pre-determined temperatures (215, 210, 190, and 150 °C), followed by air cooling (fast cooling). The joint strength of the Al/PA6 joints and the crystalline properties of PA6 after adopting the thermal processes were investigated. The strength of the Al/PA6 joints increased with decreasing the pre-determined temperatures from 215 to 190 °C and became constant when the pre-determined temperature was 190 and 150 °C. It was because the degree of crystallinity of PA6 increased with decreasing the pre-determined temperatures from 215 to 190 °C and became constant when the pre-determined temperature was 190 and 150 °C. The increase in the joint strength was attributed to the increased degree of crystallinity of PA6.

In Chapter 5, the effect of C powder composition in the Al-Ti-C powder blend on the morphology and microstructure of the anchor layer and the joint strength of the Al/PA6 joints was investigated. The molar ratio of Al:Ti:C was controlled to be 1:1:M_C (M_C = 0, 0.4, 0.6, 0.8, 1.0, and 1.5). The structure of the anchor layer was evaluated quantitatively in terms of bonding ratio and projected area fraction. In the case of low C content ($M_C \leq 0.6$), Al_3Ti phase preferentially formed at the interface between the anchor layer and the A5052 substrate, enhancing the formation of metallurgical bonding. The chemical reaction between Ti powder and the Al substrate formed the Al_3Ti phase at the interface. However, when C content was too low (M_C = 0.4), the granular protrusions were submerged into the Al substrate due to the excessive chemical reaction at the interface. With increasing C content, Al_4C_3 phase preferentially formed instead of the Al_3Ti phase ($M_C \geq 0.8$), leading to poor bonding between the anchor layer and A5052 substrate. The projected area fraction changed depending on M_C and the formation of TiC phase because the TiC phase forms the skeleton structure in the granular protrusion. The Al/PA6 joint via the anchor layer with high projected area fraction and high bonding ratio exhibited remarkable joint strength. This was because the anchor layer provided rigid sufficient sites for interlocking with PA6 and resisted high external force.

In Chapter 6, the energy density of the laser irradiation changed by adopting different laser scan speed and power to fabricate the anchor layer. Changes in the morphology and microstructure of the anchor layer and the mechanical characteristics of the Al/PA6 joints were investigated. The laser powers were controlled to be 300 and 400 W, while the laser scan speeds were controlled to be

10, 30, 50, 70, and 100 mm/s. The structure of the anchor layer was quantified in terms of the bonding ratio and projected area fraction of the anchor layer and width, height, and aspect ratio of the granular protrusions. The quantities representing the anchor structure correlated with a laser energy density. The quantitative evaluation revealed that the structure of the anchor layer changed significantly at the laser energy density of 10 J/mm. It was found from the microstructure observation of the anchor layers that the chemical reaction between the Al-Ti-C powder blend and Al alloy substrate occurred remarkably when the laser energy density was larger than 10 J/mm. The above findings suggest that the changes in the anchor structure were derived from the chemical reaction between the Al-Ti-C powder blend and Al alloy substrate. The joint strength of the Al/PA6 joints changed significantly depending on the structure of the anchor layer. In addition to the quantities representing the bonding ratio and projected area fraction, the aspect ratio contributed to enhance the joint strength. The anchor layer consisted of the granular protrusions with high aspect ratio were beneficial to withstand the external stress adopted to the Al/PA6 joint via the anchor layer since the entangled volume with PA6 increased when the granular protrusions with high aspect ratio were utilized.

The thesis was summarized in Chapter 7. The process conditions including the powder type, powder blend ratio, and laser parameters for fabricating the anchor layer significantly influenced the structure of the anchor layer. The thermal joining conditions for manufacturing metal/semi-crystalline polymer hybrid structures were important since the thermal conditions influenced the characteristics of the polymer. The structural characteristics of the anchor layer for high joint strength were revealed. The bonding ratio and projected area fraction of the anchor layer and aspect ratio of the granular protrusion indicated a positive influence on enhancing the joint strength. The joint strength was compared with previous metal/polymer direct joining researches. Considering the strength of polymer materials used in the previous researches, the anchor layer induced the anchor effect most efficiently. Finally, future issues for the development of the metal/polymer direct joining via the anchor layer were proposed.