Surface Treatment Technologies of Aluminum Alloy for Automobiles

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Light materials, such as aluminum alloy sheets, are increasingly being used for the purpose of reducing weight in automotive bodies. Regarding the surface characteristics required for such aluminum alloy sheets, emphasis is being placed, especially in Europe, on bonding durability to suppress the deterioration of joints bonded using adhesive in environments such as salt water spray conditions. Titanium/zirconium (Ti/Zr) treatment is a surface treatment adopted by automotive manufacturers outside Japan to improve the bonding durability of automotive aluminum materials. In Europe, electric discharge texturing (EDT) surfaces, as well as dry lubricant, are being used in addition to Ti/Zr treatment. In order to use materials that are surface treated in accordance with European specifications, the process conditions, including conversion coating, must be optimized. Kobe Steel can provide Ti/Zr treatment, EDT surfaces and dry lubrication.

Introduction

With a social need to improve the fuel consumption of automobiles as a climate change mitigation measure, light materials, such as aluminum alloy sheets, are increasingly being used for reducing the weight of automotive bodies, which would be a promising measures for that purpose. Surface characteristics required for aluminum alloy sheets for automotive panels include weldability and the ability to be lubricated for forming. It is necessary to uniformly apply conversion coating, such as zinc phosphate treatment, to provide acceptable painting quality and corrosion resistance, and thereby requiring the ability to be degreased and chemical treatability. On the other hand, emphasis is now being placed, especially in Europe, on bonding durability to suppress the deterioration of joints bonded using adhesive in environments such as salt water spray conditions. Bonding with adhesive is positioned as a secondary measures for mechanical joining or welding; however, it contributes also to improvement in rigidity, safety in collisions, and NVH properties (Noise, Vibration, and Harshness). In order to improve the bonding durability of joints bonded using adhesive, a surface treatment to suppress the deterioration of the interface between adhesive and base material has been developed.

This paper evaluated the characteristics of Ti/Zr treatment as applied to Kobe Steel's products, a treatment which is extensively used especially in Europe to improve bonding durability. It examined also the application of the Electron Discharge Texturing (hereinafter referred to as EDT) method to our products, a method which controls dry lubrication and surface roughness to improve the ability to be lubricated. The results are reported below.

1. Ti/Zr treatment

Generally in Japan, aluminum alloy sheets for automotive panels are subject to acid pickling, etc. to remove the oxide film generated in the annealing process,[2] and then shipped as raw material. By contrast in Europe, Ti/Zr treatment is applied at the raw material stage as a surface treatment, in addition to such acid pickling treatment, etc.[1), 3)] Ti/Zr treatment is a technology that has been extensively used by overseas automotive manufacturers, including German-affiliated companies, and it features oxide films of Ti/Zr formed on the surface of aluminum alloy with oxide film removed, using oxide hexafluoride of Ti and Zr.[4] The film formed on the surface is known not to interfere with formability, weldability, and zinc phosphate treatability, in addition to its contribution to improving bonding durability.

1.1 Ti/Zr treatment process

Fig. 1 shows the manufacturing and processing process of aluminum sheets for automotive panels from the viewpoint of the technologies related to surface treatment. **Fig. 2** shows the Ti/Zr treatment process that is performed in the surface treatment process shown in Fig. 1. Heat-treated cold-rolled coils require the removal of oxide film, in advance, through acid pickling to be performed after alkaline degreasing. Ti/Zr coating is then formed by spraying a chemical agent for Ti/Zr treatment and thereafter rinsing and drying. We formed the Ti/Zr coating using Gardobond® X4591 provided by Chemetall as a chemical agent for Ti/Zr treatment. **Fig. 3** shows the cross-sectional observation photo of this Ti/Zr coating. This photo shows that an oxide film of

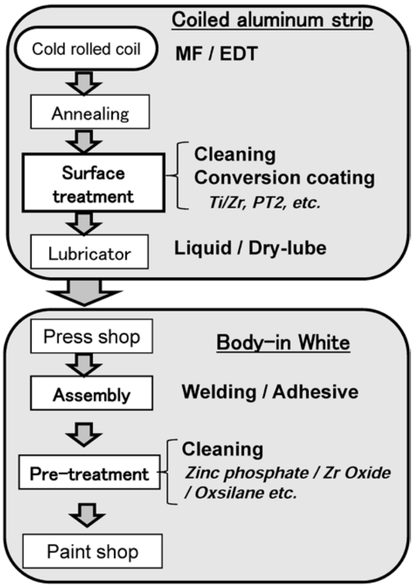

Fig. 1 Manufacturing process of automotive aluminum sheets (surface related technology)

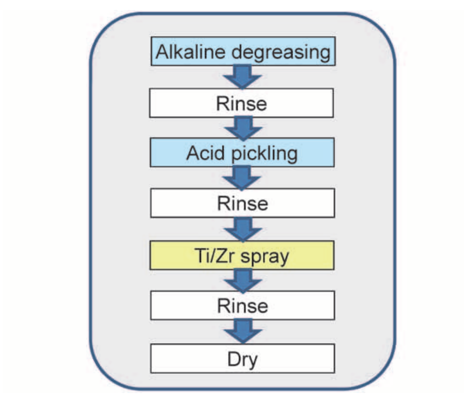

Fig. 2 Process flow of surface treatment for coiled aluminum strips

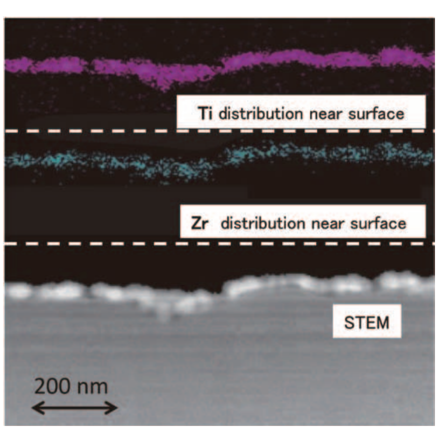

Fig. 3 Cross-sectional image and distribution of Ti, Zr in Ti/Zr conversion coating

several tens of nanometers in thickness containing Ti and Zr has been formed.

1.2 Bonding durability and hydration of Ti/Zr coating material

Fig. 4 shows the evaluation results of bonding durability after salt spray tests for 3,000 hours using our 6022 alloy both with Ti/Zr coating and with acid pickling and rinsing only (hereafter referred to as material with cleaning only). Specimens for shear tests were manufactured using epoxy resin based adhesive, zinc phosphate electrodeposition coating was applied, and then shear tests were performed before and after durability tests. The results revealed that the material with Ti/Zr coating scarcely decreases in its cohesive failure rate and adhesive bonding strength, but is superior in bonding durability, when compared with the material with cleaning only.

Factors in the deterioration of bonding durability in the interface between adhesive and aluminum base material include the hydrated oxide produced on aluminum surfaces when moisture penetrates and is diffused near the interface.[1] **Fig. 5** shows the

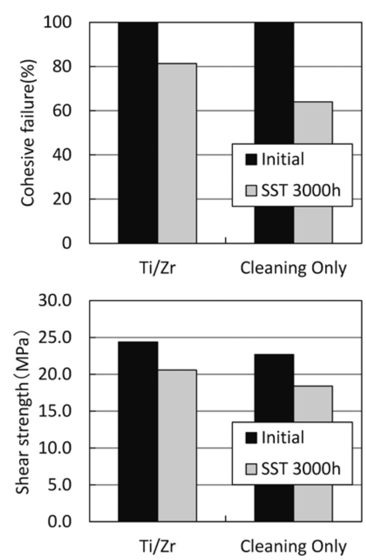

Fig. 4 Adhesive durability (cohesive failure ratio and shear strength) of 6022 alloy with and without Ti/Zr coating

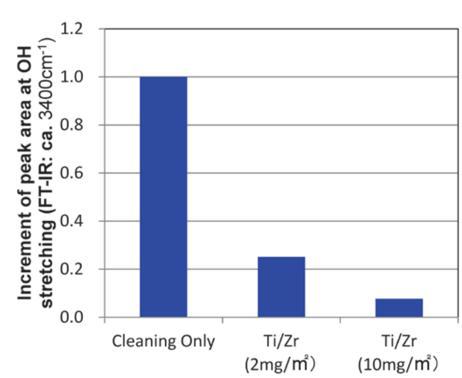

Fig. 5 Influences of Ti/Zr coating on hydration (50℃, 95%RH, 24 hrs)

influences of Ti/Zr coating on hydration. Ti/Zr coating proves that, once formed, it suppresses hydration on the base material surface that is equivalent to a bonding interface. It would appear that this difference in hydration behavior corresponds to bonding durability[5)].

1.3 Influence of Ti/Zr coating on zinc phosphate treatment, filiform corrosion resistance, and weldability

The influence of Ti/Zr treatment on zinc phosphate treatment and filiform corrosion resistance was evaluated using 6022 alloys and general test conditions. **Fig. 6** shows the observation results of the change in the film weight of zinc phosphate coating and its morphology when varying the amount of fluoride in a zinc phosphate treatment bath, for both materials with Ti/Zr coating and with cleaning only. The results reveal that the material with Ti/Zr coating has achieved a zinc phosphate treatability equivalent to that of the material with cleaning only. However, the film weight of the zinc phosphate coating may decrease in the case of material with a large film weight of Ti/Zr coating, or depending on the conditions of zinc phosphate treatment. While chemical agents for other than zinc phosphate treatment have been used as environmental measures[6), 7)], it seems that the chemical agent for Ti/Zr treatment can be applied in place of these various chemical agents by adjusting the treatment conditions.

Fig. 7 shows the filiform corrosion test results of material with zinc phosphate treatment and electrodeposition coating. The results revealed that the material with Ti/Zr coating achieves basically the same filiform corrosion resistance as the material with cleaning only.

Fig. 8 shows the MIG and laser welding tests results for the weldability evaluation using Kobe Steel's 6016 alloy. During tensile tests, every specimen was fractured in the base material but not in the weld, showing that the level of strength was the same. It thereby proved that the material with Ti/Zr coating achieves the weldability equivalent to that of the material with cleaning only.

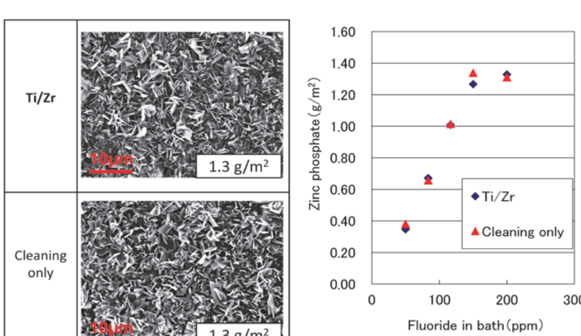

Fig. 6 Surface morphology and film weight of zinc phosphate coating

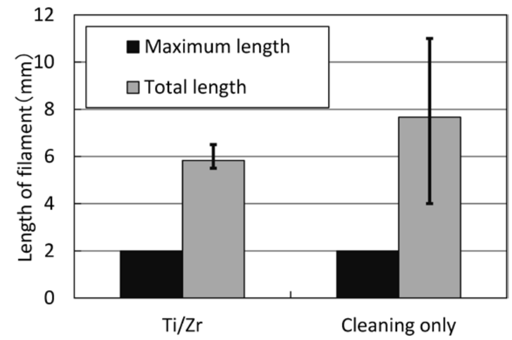

Fig. 7 Filiform corrosion test results of materials with and without Ti/Zr coating after 8 cycles
Cycle: SST 35℃×24 hrs−40℃, 85%RH×120 hrs−r.t. 24h

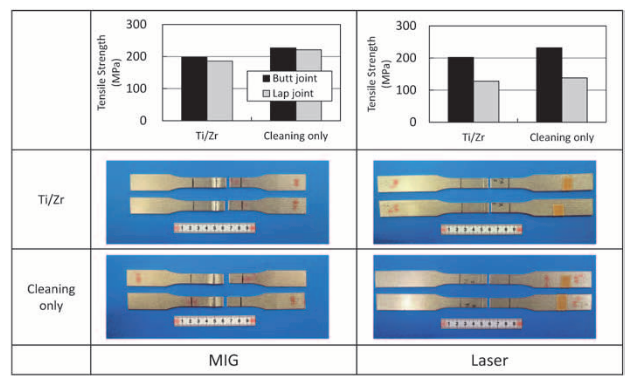

Fig. 8 Tensile strength test after welding

2. EDT and dry lubrication

2.1 Control of surface roughness by EDT

Mill Finish (hereinafter referred to as MF) material is used in Japan, whereas EDT material is extensively used in Europe. EDT features surface morphology formed by rolling with rolls that were dull electric discharge machined. **Fig. 9** shows the comparison of the surface morphology in 6022 alloy between EDT and MF. The surface morphology with EDT has no rolling line, indicating that it is a morphology having irregularity without anisotropy.

When dry lubrication is used, which will be described at a later stage, two sheets may adhere to each other in a destacking process, in which stacked aluminum sheets are lifted. However, it is known that the material surface morphology with EDT suppresses adhesion, thereby improving the workability in the destacking process.[3)] The advantage of dry lubrication includes behavior that eliminates the influence of forming direction in the

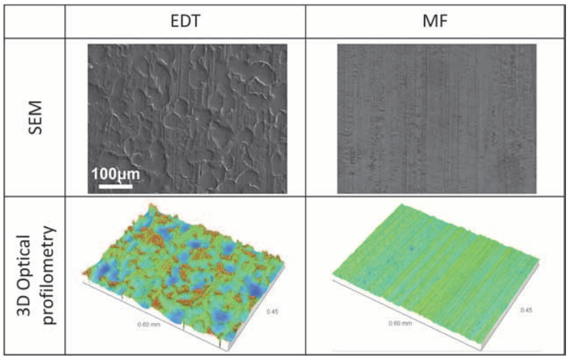

Fig. 9 Comparison of surface morphology between EDT and MF

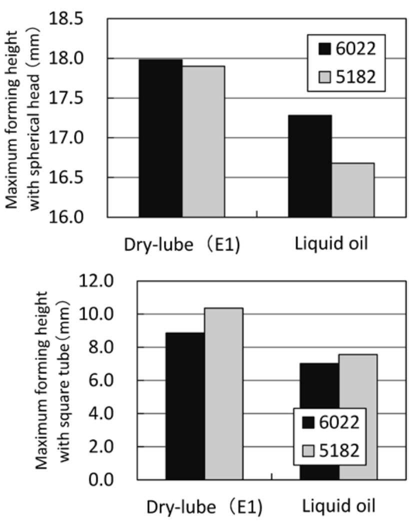

Fig.10 Influence of dry lubrication on punch stretch forming (using spherical head (φ50mm) and square tube (50mm))

forming process, allows lubricant to be retained more easily, thereby contributing to improvement in formability, eliminating anisotropy in the appearance after coating, etc.[8)]

2.2 Improvement in formability through applying dry lubrication

In order to improve formability, paraffin wax, surfactant, etc. with a melting point of about 40 to 50℃ are used as dry lubricant. In various methods, dry lubricant is applied mostly by heating, melting, and then electrostatic spraying. **Fig.10** shows the formability when dry lubricant E1 from Zeller + Gmelin is used with 6022 alloy and Kobe Steel's 5182 alloy. The results reveals that excellent punch stretch forming height and drawing height are achieved when compared with using liquid oil. On the other hand, dry lubricant is inferior in its capacity for being degreased; therefore, dry lubricant could not be removed sufficiently using the same degreasing conditions as are used for liquid oil. It appears that when dry lubricant is applied it is necessary to adjust the concentration and temperature of a degreasing bath.

Conclusions

Ti/Zr treatment is a surface treatment adopted by automotive manufacturers outside Japan, and it improves bonding durability of aluminum material for automobiles. In Europe, EDT surfaces, as well as dry lubricant, are being used in addition to Ti/Zr treatment. Not only in Europe but also in North America, there is a need to improve bonding durability, and chromium-free PT2 consisting of colloidal silica (developed by Novelis), ALCOA951 consisting of organic components, and new surface treatment, such as thin film anodic oxidation, also beginning to be applied, and they are currently supplied to overseas automotive manufacturers.[1)] However, when such "surface treatment agent for overseas use" is used in Japan, optimized conversion treatment conditions are required. Kobe Steel therefore promotes the development of the surface treatment technology that corresponds to the surface treatment conditions used in automotive manufacturers in Japan. Kobe Steel can provide Ti/Zr treatment material, and EDT and dry lubrication treatment materials.

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