

Development of Seal Technology for Electric Double-layer Capacitor Covers Using Aluminum-Resin Insert Mold Process

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ABSTRACT

Electric double-layer capacitor covers are required to seal in organic liquid electrolyte, to isolate positive and negative electrodes, and to maintain pressure tightness. An insert mold process using chemically combined aluminum and resin and a rib to prevent resin shrinkage have been developed to enable these requirements to be met. In this process aluminum and resin are bonded by insert molding after triazinedithiol electrocoating of the aluminum surface. Optimization of the formation of the triazinedithiol coat and insert mold conditions and the establishment of a rib between the aluminum and resin have enabled the production of covers which satisfy the requirements enumerated above after acceleration tests based on actual use conditions. The long-term sealing performance of the new covers has also been verified.

1. Introduction

The Honda FCX fuel cell vehicle, which was first commercially produced in December 2002, employs an electric double layer capacitor module as an energy storage system. Because the functioning of the capacitors does not involve a chemical reaction, they display higher power output and superior durability towards repeated charge and discharge than batteries. Together with the fuel cell utilized in the FCX, the new capacitors represent a clean energy

technology with considerable future potential. The case cover employed in the capacitors was required for reliability against the leakage of electrolyte, for the maintenance of internal pressure of the cells, and for the ability to maintain electrical insulation of the positive and negative electrodes.

The insulating and sealing functions of the case cover are vital to ensuring the reliability of the capacitor cell. This paper will discuss the world's first application of insert molding to a capacitor case cover, and describe the methods used to verify the reliability of the new cells.

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2. Development Concept

2.1. Factors Affecting Reliability

The design concept for the capacitor to be employed in the FCX specified a cylindrical shape. The continuing reliability of the seals over long-term use represented another requirement.

Among normal round case covers, aluminum electrolytic condenser covers offered a potential design precedent, but because their structure allows the entry and escape of air, they cannot be used to seal a capacitor employing an extremely osmotic electrolyte.

The following factors were therefore established as being essential to reliability, and the capacitor case cover was developed with a strong focus on long-term reliability:

- (1) Ability to seal a highly osmotic electrolyte
- (2) Ability to insulate positive and negative electrodes
- (3) Sufficient strength to resist increases in the internal pressure of the cell

2.2. Concepts Established for Structure and Materials

Figure 1 shows a perspective view of the capacitor case cover. (1) shows the case cover in the developmental stage, while the cover actually employed in the FCX capacitors is seen in (2). As Fig. 1 demonstrates, the shape of the covers is different, but the concept behind them is the same, in that the outer circumference represents the negative electrode and the center terminal the positive electrode. Aluminum is used for both the outer circumference and the center terminal, with resin employed as an insulating material between them. The outer circumference forming the negative electrode is welded to the cylindrical case, and the terminal representing the positive electrode is welded to the electrode collector plate. This configuration led to the selection of high-purity and high-strength A3003-H112 as the material, to enable both welding and screw-in mounting to be employed. It was essential for the resin to possess high strength in addition to insulating the positive and negative electrodes. The thermoplastic resin polyphenylene sulfide (PPS) was therefore selected, from considerations of heat resistance to enable high-temperature curing in the production process, to remove impurities from the electrode, resistance to organic liquid electrolytes, the ability to form compounds with triazinedithiol (as discussed in section 3), and recyclability. Glass fiber and calcium carbonate is added to the PPS in quantities optimized to coordinate its coefficient of linear thermal expansion with that of aluminum. This reduces the thermal expansion differential of the material with aluminum, even under the rapid heating of welding, ensuring that

shearing stress is not generated at the interface of the bonded aluminum and resin, and thus preventing the strength of the bond from declining.

Another reason for mixing glass fiber with the PPS is to increase the material's breaking strength. Glass fiber is anisotropic with regard to contraction after formation, with low contraction in the direction of orientation of the fibers and high contraction in the non-orientation direction. Because formation of the case cover involves injecting resin through three gates, as shown in Fig. 2 (1), glass fiber tends to become oriented around the circumference. Therefore, there is a large post-formation radial contraction, generating shearing forces at the interface of the aluminum and resin, which cause the bond to break down. Once the bond has commenced breaking down, the release of residual stress continues to progress, forming paths through which the electrolyte can leak. To prevent this, 1 mm high ribs are positioned on the positive and negative electrodes to function as resin stoppers and prevent contraction of the resin, as shown in Fig. 2 (2). This reduces post-formation residual stress to zero, ensuring long-term reliability. The presence or absence of the ribs significantly affected the results of the acceleration tests discussed in section 5.

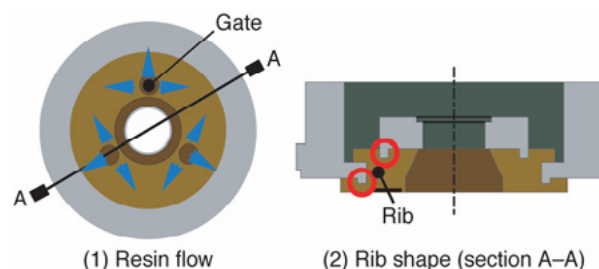


Fig. 2 Resin flow and rib shape

3. Process Concept and Characteristics

3.1. Conventional Resin Insert Molding

In the conventional resin insert molding process, resin is poured into a metal mold after insertion of the aluminum parts, and contraction of the resin forms a physical bond between the aluminum and the resin.

3.2. Concept behind New Process

The newly developed production process is divided into

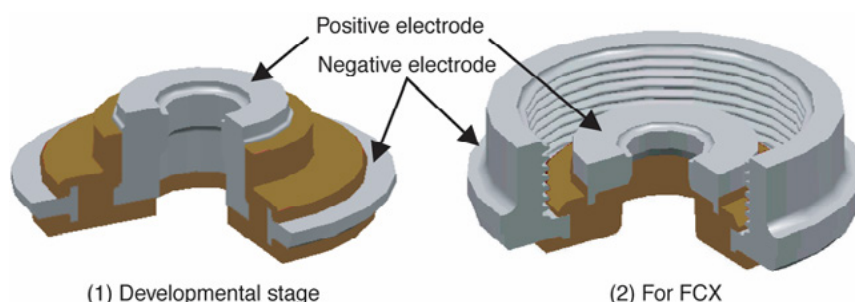


Fig. 1 Perspective view of cover

three stages: Cutting of the aluminum parts to be inserted in the mold, a surface treatment process in which triazinedithiol is electrodeposited to create a chemical bond between the aluminum and the resin, and the molding process, in which the resin is injected into the mold, producing the finished case cover. Figure 3 illustrates the difference between this process and the conventional process. The innovation in the new process is the addition of surface treatment (triazinedithiol treatment).

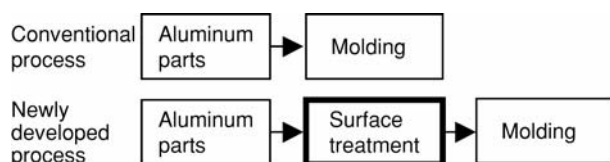


Fig. 3 Comparison of insert mold processes

3.2.1. Cutting

The aluminum employed in the outer circumference of the case cover and the terminals is conventionally rolled and cast, after which it is cut to the required dimensions. The change in dimensions during etching in the surface treatment process and the changes occurring due to contraction in the forming process must be taken into consideration in this initial process.

3.2.2. Surface treatment

To activate the aluminum surface, it is neutralized with acid after alkali etching. It is then subjected to triazinedithiol electrocoating treatment (organic coating), after which drying under reduced pressure represents the final stage of the process (Fig. 4).

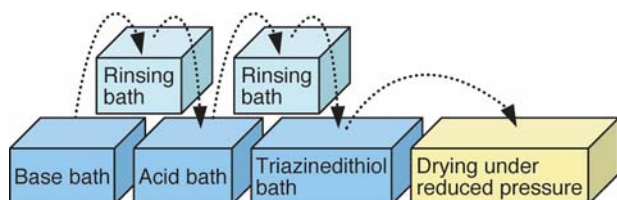


Fig. 4 Treatment process

In the electrocoating process, a film of approximately 150–250 nm is formed by bonding of the triazinedithiol with the positively charged side of the aluminum and the formation of bonds between triazinedithiol molecules, as shown in Fig. 5⁽¹⁾.

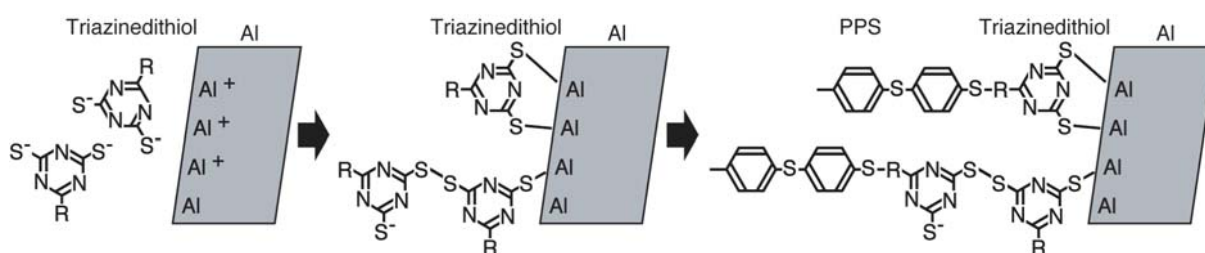


Fig. 5 Sealing mechanism aluminum-triazinedithiol-resin

3.2.3. Molding

Having undergone surface treatment, in the forming process the aluminum parts are inserted into a metal mold into which PPS is then injected. The sulfur and R components in the triazinedithiol chemically bond with the sulfur in the PPS, forming a seal at the interface of the aluminum and the resin and unifying the outer circumference, resin and terminals.

The adhesive strength of the formed product varies greatly with conditions during production. The factors affecting the adhesive strength are the ease of chemical bonding between the functional groups in the film and the PPS, and the soundness of the weld at the interface of the melted PPS. The ease of chemical bonding is increased by raising the temperature, and increased pressure guarantees the soundness of the resin. However, if the temperature of the mold is increased too much, expansion of the aluminum causes galling with the mold, and too great an increase in the internal pressure of the mold causes deformation of the aluminum parts. Optimization of the conditions has enabled a balance to be maintained in the molding process.

3.3. Analysis of the Film during Triazinedithiol Treatment

It has conventionally been difficult to observe the condition of the film without damaging it. In this project, the following method was used to examine the condition and thickness of the film:

First, after coating with platinum to prevent surface damage to the film, test cross-sections were irradiated by a gallium ion beam (focusing ion beam: FIB). They were then observed using a field emission scanning electron microscope (FE-SEM). Results showed that uniform triazinedithiol layers of approximately 200 nm with no pinhole imperfections had been formed on the aluminum (Fig. 6).

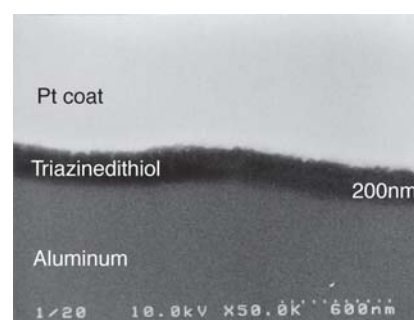


Fig. 6 Cross-section of aluminum and triazinedithiol layer

3.4. Characteristics of the New Process

The high adhesive strength ensured by the firm chemical bond between the aluminum and resin achieved in this process is highly durable towards increases in internal pressure, which may be caused by changes in temperature, etc., during operation of the cell. A reliable seal is formed, ensuring insulation and preventing shorting caused by leakage of the extremely osmotic electrolyte.

Another advantage of the new production process is that the use of insert molding means that there is little restriction on the shapes that can be formed.

3.4.1. Film specifications

As Fig. 7 shows, film thickness increases with treatment time. A stable film is formed after a specific period of time, enabling the establishment of a treatment time guaranteeing the viability of the film.

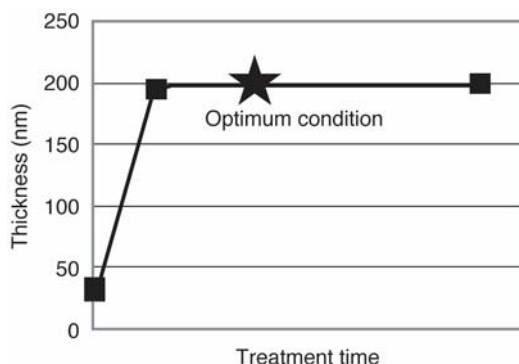


Fig. 7 Thickness of triazinedithiol coating

There is a great deal of aluminum and oxygen in the film that is formed, and traces of sulfur and carbon of triazinedithiol have also been detected (Fig. 8).

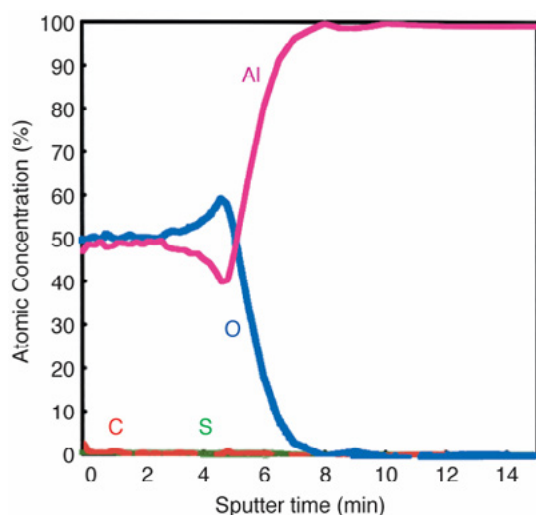


Fig. 8 AES analysis of triazinedithiol coat

3.4.2. Base conditions for molding

Conditions for molding were optimized as shown in Fig. 9, to prevent galling or deformation of the aluminum parts and produce high adhesive strength. Figure 10 shows a cross-section of a case cover formed under these conditions. It is clear that a reliable bond has been formed between the aluminum parts and the resin.

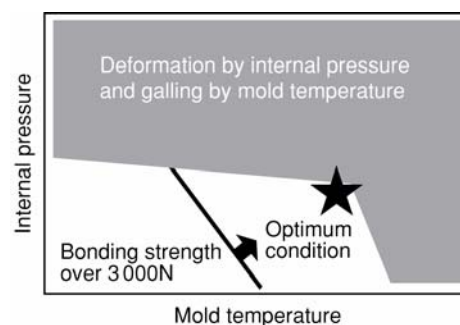


Fig. 9 Insert mold condition



Fig. 10 Cut section of cover

4. Verifying the Quality of the Seal

4.1. Concepts behind Verification

4.1.1. Chemical verification

According to Arrhenius' principle (Eq. 1), the speed of a simple reaction is normally dependent on temperature. If the temperature increases 10 K, the reaction speed doubles.

$$k = A \exp(-Ea / RT) \quad (1)$$

k : Reaction speed

A : Frequency factor

Ea : Activation energy

R : Gas constant

T : Absolute temperature

To determine whether the degradation of the strength of the new case cover obeyed Arrhenius' principle, units were immersed in electrolyte liquid at different temperatures, and the time taken for a 20% decline in adhesive strength to occur was plotted. The results of these tests are shown in Fig. 11, and verify that the strength of adhesion in the case cover degrades in accordance with Arrhenius' principle. High-temperature acceleration tests were conducted on the basis of these results to determine whether the functional life of the cover would satisfy automotive requirements and no malfunctioning of the seal was demonstrated. The quality of the seal remained excellent even under acceleration tests corresponding to 1.5 times the life of the vehicle.

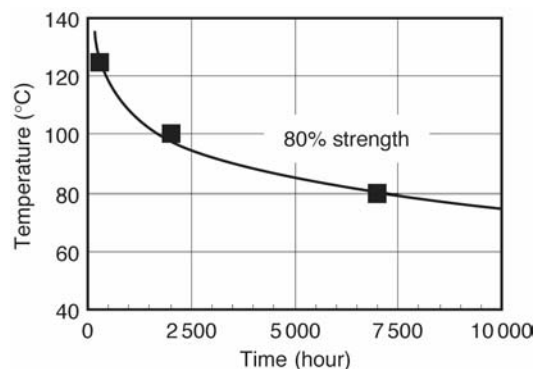


Fig. 11 Degradation of bond strength

4.1.2. Mechanical verification

The conditions established for mechanical verification of seal quality are that the seal should show no change after thermal shock or vibration. Thermal shock characteristics were measured by putting a case cover through the thermal cycle shown in Fig. 12 1,000 times. To test characteristics under vibration, test equipment was used to subject the covers to prescribed levels of vibration. The seal demonstrated no change in quality after either of these tests.

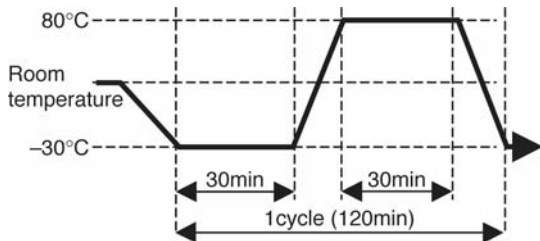


Fig. 12 Thermal shock test cycle diagram

4.2. Quality Inspection

One major issue in the production process is to ensure that the seals that allow electrolyte to leak do not get through the system. Three tests are used to inspect quality during production: Measurement of the infrared spectrum to analyze the components of the film after surface treatment, ultrasonic inspection to enable non-damaging inspection of the adhesion, and pressure inspection to check seal quality and pressure resistance.

After completion of surface treatment of the aluminum parts, the infrared spectrum is measured using a Fourier transform infrared spectrophotometer. The absorbance of the triazinedithiol is measured in the $1,125\text{ cm}^{-1}$ absorption band, enabling confirmation that the film has been formed according to specifications.

After forming, the completed product is inspected using an ultrasonic detector, as shown in Fig. 13. Ultrasonic inspection examines for structural imperfections through separate inspection of the bonded sections of the outer circumference and terminals. This method is used to inspect for pinholes and micro-cracks in the welded sections. Measurements taken using this method were cross-referenced with measurements from other equipment and compared with test data to confirm that it was sufficiently accurate to evaluate the soundness of the interface between the aluminum and the resin.

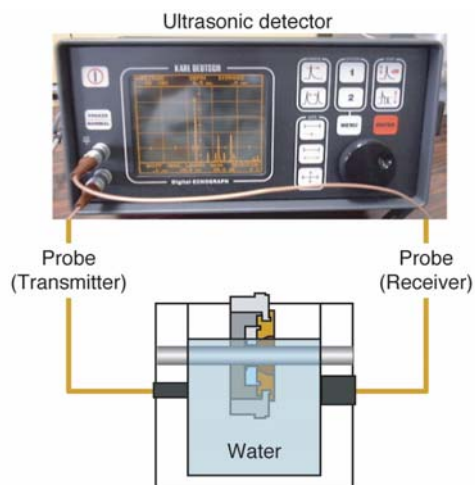


Fig. 13 Ultrasonic inspection

Pressure inspection utilized the set-up shown in Fig. 14, and verified that there were no paths for potential leakage under a back pressure of 5 MPa.

These three inspection methods effectively prevent faulty units from going into distribution.

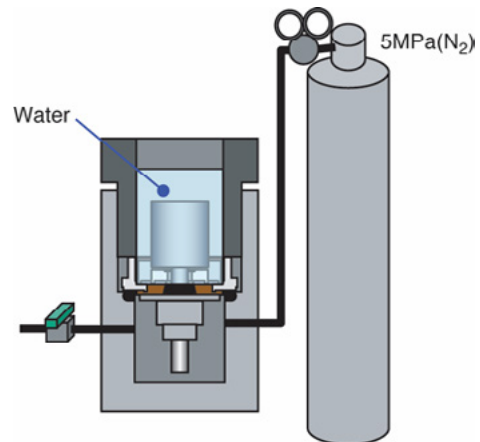


Fig. 14 N₂ pressure inspection

5. Results of Durability Evaluation

5.1. High-temperature Electrolyte Immersion Test

Figure 15 shows the results of measurements of bond strength after the acceleration test discussed in section 4. The units maintained a high level of bond strength. The absence of any paths for leakage to occur in the interface between the aluminum and resin, as shown in Fig. 16, confirms that the seal will remain viable for the life of the vehicle.

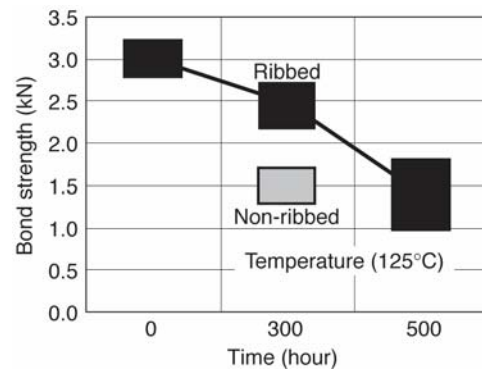


Fig. 15 Bond strength after acceleration test

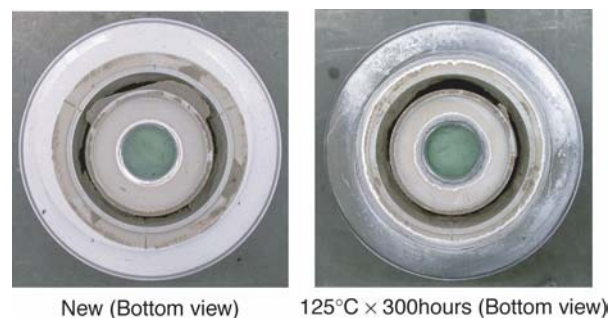


Fig. 16 Adhesion condition after acceleration test

6. Summary

An insert molding process has been developed and utilized for the production of capacitor case covers for the first time in the world. The aluminum parts used are fitted with ribs to prevent contraction of the resin. Electrocoating of triazinedithiol at the interface of the aluminum and resin has enabled the achievement of a very reliable bond, and the applicability of this process to capacitor case covers was verified.

The reliability of the cover has been ensured by optimization of the conditions for treatment of the triazinedithiol and the insert mold conditions during forming, and by post-formation analysis of the composition of the film, ultrasonic inspection and pressure testing. In addition to acceleration testing, methods of analysis of the condition of the ultra-thin film (which has conventionally been difficult) and of degradation of the strength of the bond have also been developed.

Acknowledgments

In closing, the authors would like to take the opportunity to thank all those, representing Honda and other companies, who contributed to the success of this project.

Reference

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