High-temperature, High-pressure Warm Isostatic Pressing Equipment for All-solid-state Battery Manufacturing Process

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Abstract

In the manufacturing process of all-solid-state batteries, pressure treatment is performed to form the interface between the electrode active material and the electrolyte. Warm isostatic pressing (WIP) technology has potential application in the pressure treatment process because it can isostatically pressurize target materials at high temperatures and pressures. However, the optimal processing pressure and temperature remain unclear for all-solid-state batteries. Accordingly, Kobe Steel has been researching the densification of all-solid-state battery electrodes using WIP technology, aiming to adopt it in the all-solid-state battery manufacturing process. The company is also developing equipment to perform WIP treatment at higher temperatures. This study demonstrates that a good electrode interface can be obtained by performing WIP treatment at a high temperature and pressure. Furthermore, heating the pressure medium inside the high-pressure piping of the WIP equipment improves the temperature distribution inside the pressure vessel. This is expected to reduce temperature variations during the processing of all-solid-state batteries, thereby improving battery quality when performing WIP treatment at high temperatures. This paper discusses the results of this research and equipment development.

Introduction

Warm isostatic pressing (WIP) simultaneously applies high temperature and high pressure to workpieces, using a liquid heated to a high temperature as the pressure medium. WIP technology has been utilized in various applications, including the pressure bonding of multilayer ceramic capacitors, and Kobe Steel has long history of providing WIP equipment in many applications.

Recent research has shown the possibility that WIP technology can be applied to the manufacturing process of all-solid-state lithium-ion batteries. All-solid-state batteries are composed entirely of solid materials; therefore, pressure treatment is performed to eliminate voids between the electrode active material (AM) and solid electrolyte (SE) and to improve adhesion. Research on pressure treatment has reported that simultaneous heating and pressurizing enhances the fluidity of the SE and is effective for forming a good interface.[1)] Therefore, WIP technology is thought to be suitable as a pressurization method for manufacturing all-solid-state batteries.

However, all-solid-state batteries are still under development, including their manufacturing process, and the optimal processing pressure and processing temperature have not yet been determined. Accordingly, Kobe Steel is advancing research on how WIP processing temperature and pressure affect the structure and characteristics of all-solid-state batteries, with the aim of adopting this technology in their manufacturing process, developing higher processing temperature capability for WIP equipment, and reducing temperature variation inside the pressure vessel.

1. Challenges of pressurization technology in all-solid-state battery manufacturing process

Eliminating voids between the electrode AM and the SE and improving adhesion are important for enhancing charge and discharge capacity and energy density for an all-solid-state battery. Uniaxial pressurization methods such as roll pressing and single-action pressing are commonly used to eliminate these voids and improve adhesion. However, microscopic irregularities on the surfaces of the electrode AM layer and SE layer prevent uniform pressurization, making it difficult to sufficiently improve the adhesion between the electrode AM layer and SE layer.[2)] By contrast, WIP technology can apply isotropic pressurization to a workpiece; therefore, it is considered possible to obtain an all-solid-state battery with superior adhesion between the electrode AM layer and SE layer by adopting WIP technology.

All-solid-state batteries are still under development, including their manufacturing process, and optimal processing pressure and temperature are not yet clear. However, it is possible that high temperatures, up to 200℃ may be required as the processing temperature. Research has reported that pressurization at a high temperature of 190℃ using WIP technology increases electrolyte fluidity and enables the formation of an interface with higher adhesion.[3)]

Kobe Steel aims to develop large-size WIP equipment for the stable mass production of all-solid-state batteries. For this purpose, it is necessary to solve issues related to increasing processing temperature and reducing temperature variation in the pressure vessel in intensifier-type WIP equipment. This paper describes the development results of intensifier-type WIP equipment compatible with 200℃ that can be applied to production machines.

2. Current status of the WIP equipment

2.1 Overview of Kobe Steel's WIP equipment

Our WIP equipment is composed of the following components:

1) Pressure vessel and top and bottom closure that retain high pressure internally
2) Press frame that supports the axial force inside the pressure vessel
3) Hydraulic pressurizing system(intensifier or piston)
4) High-pressure valves that hold and release pressure medium
5) Jacket and heating equipment that heat the pressure vessel

With these components, the pressure vessel is filled with the pressure medium and heated; then, the workpiece is inserted and pressure is increased using the pressurization mechanism. This process creates a high-temperature, high-pressure state inside the pressure vessel, thereby applying isostatic pressure to the workpiece.

2.2 Advantages and challenges of pressurizing system for WIP equipment

WIP equipment is classified as intensifier or piston type depending on the pressurization method. **Fig. 1** compares each pressurization method in WIP equipment, and the characteristics, advantages, and challenges of each method are listed in **Table 1**. The intensifier type is a method in which the pressure medium is fed into the pressure vessel by an intensifier to increase pressure, and it is mainly adopted in medium to large machines with processing pressures of 600 MPa or less. By contrast, the piston type is a method in which the pressure medium is directly compressed by pushing a piston into the pressure vessel and is mainly adopted in small machines with processing pressures exceeding 600 MPa. The intensifier type is more suitable for increasing the diameter of the pressure vessel compared to the piston type, but the temperature of the pressure medium supplied to the intensifier

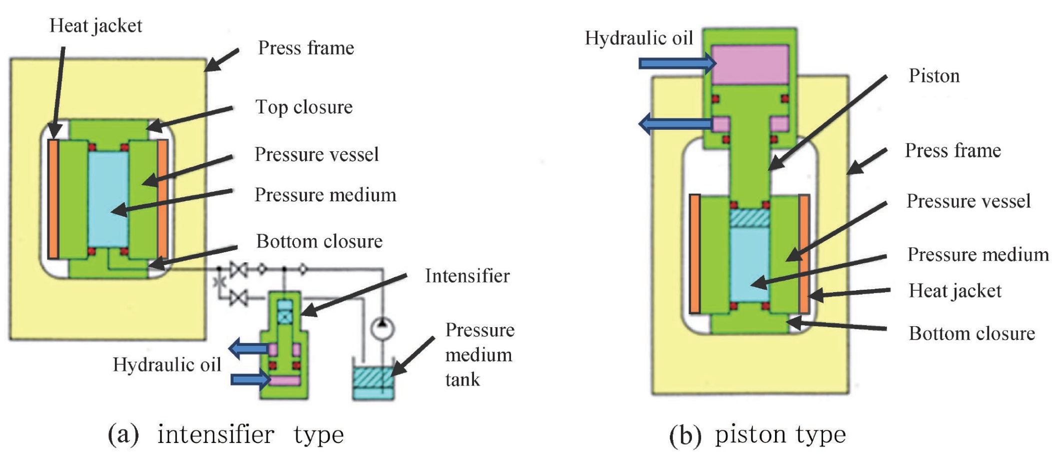

Fig. 1 Comparison of pressurizing system for WIP: (a) intensifier type and (b) piston type

Table 1 Advantages, and challenges of each pressurizing system for WIP

Pressurizing system	Intensifier type	Piston type
Inner diameter	Medium to large	Small
Pressure level	Low (600 MPa or under)	High (over 600 MPa)
Advantage	Suitable for large scale (diameter) WIP	Easy to achieve high temperature and high pressure in pressure vessel
Challenge	Difficult to achieve high temperature and prevent occurring temperature distribution	Not suitable for large scale (diameter) WIP

is limited to 80℃ depending on the heat resistance temperature of the intensifier high-pressure seal. As a result, even if the pressure medium inside the pressure vessel is heated before pressurization, low-temperature pressure medium flows into the pressure vessel, causing temperature differences inside the pressure vessel after pressurization. When temperature differences occur inside the pressure vessel, variation in processing temperature arises in the workpiece inside the pressure vessel. Furthermore, even if an attempt is made to increase the processing temperature inside the pressure vessel, the temperature of the pressure medium supplied to the intensifier cannot be raised, leading to increased temperature differences inside the pressure vessel during pressurization.

2.3 Development strategy

Kobe Steel's development strategy is to develop intensifier-type WIP equipment, which is more suitable for larger diameter, with future mass production of all-solid-state batteries. And furthermore, the strategy is to develop technology that increases processing temperature and reduces variation in processing temperature inside the pressure vessel.

3. Verifying application of WIP through trial densification of cathode for all-solid-state batteries

First, an attempt was made to verify whether densification of the cathode for an all-solid-state battery is possible using WIP technology. In all-solid-state batteries, the AM has a structure in which it is mixed with the SE and additives. In this study, $Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$ (NMC) with a surface coating of $LiNbO_3$ was used as the AM, and Li_6PS_5Cl was used as the SE. The AM, SE, and conductive additive (AB) were mixed at a ratio of 74 : 23 : 3 (wt%), made into a slurry by adding binder and solvent, coated onto Al current collector foil, and dried to form the electrode. Finally, it was sealed in an aluminum laminate film to prevent contact with the atmosphere. The piston type was used for WIP treatment. The processing pressure was set to 600 MPa, processing temperature to 190℃, and processing time to 1 min. Synchrotron X-ray-Computed-Tomography (CT) was used to nondestructively evaluate the three-dimensional structure of the obtained electrode. X-ray CT measurements were conducted at SPring-8 BL16B2 (proposal numbers 2021A5320, 2021B5320, and 2022A5320). The incident X-ray energy was 30 keV. Xsight Micron LC was used to acquire X-ray CT data. The voxel size of the X-ray CT data was 1.3 μm or 0.65 μm. The sample was sealed in a glass capillary inside a glove box under an Ar atmosphere. Threshold values were determined based on the CT values of each component, and the obtained CT images were classified into three regions (AM, SE, and voids/AB/binder) to evaluate structural differences.

Fig. 2 shows CT images inside the electrode and analysis results by three-value segmentation before WIP treatment and after WIP treatment (room temperature (Approximately 20℃) or 190℃). From Fig. 2, it was confirmed that voids, AB, and binder (black) present within the electrode SE (red) decreased due to WIP treatment. This result shows that WIP treatment at a processing pressure of 600 MPa and processing temperature of 190℃ is effective for the densification of the electrode with the mixing ratio used in this study.

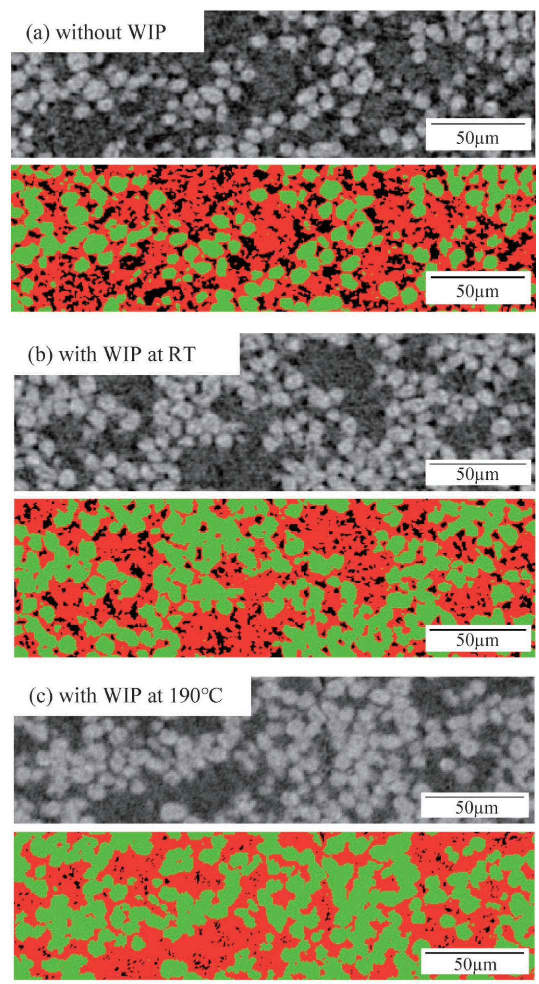

Fig. 2 CT (upper) and the categorized (lower) images of the composite electrodes. (a) without WIP, (b) with WIP at room temperature (RT), and (c) with WIP at 190℃. (NMC: green, SE: red, and voids/carbon/binder: black) The samples of (b) and (c) were pressed at 600 MPa for 1 min.

4. Study of methods for increasing temperature and reducing temperature variation using intensifier-type WIP equipment

4.1 Challenges and solutions in intensifier-type WIP equipment

As described above, in intensifier-type WIP equipment, low-temperature pressure medium flows into the pressure vessel during pressurization, which causes the inhibition of temperature increase and generation of temperature variation. This issue was addressed by applying heat exchange technology to high-pressure piping ("high-pressure heat exchange technology"). A system diagram adopting high-pressure heat exchange technology is shown in **Fig. 3**.

In this technology, the pressure medium inside the high-pressure piping is heated, enabling high-temperature pressure medium to flow into the pressure vessel. This approach in turn maintains a high-temperature state inside the pressure vessel after pressurization and reduces temperature variation.

4.2 Confirmation of effect of high-pressure heat exchange technology

4.2.1 Experimental details

Operating conditions were set such that the pressure inside the pressure vessel was 600 MPa and the pressure medium temperature was 200℃, and pressurization operation was carried out while changing the heat exchange system temperature conditions to confirm the effect of high-pressure heat exchange technology. The specifications of the test equipment used in this experiment are given in **Table 2**, and the experimental conditions are shown in **Table 3**. The heat exchange system temperature was set to 60 (Case 1) and 200℃ (Case 2), and temperatures at different height position during pressurization operation were measured using thermocouples installed at the lower, middle, and upper parts inside the pressure vessel. The thermocouples were installed at positions not in contact with the inner surface of the pressure vessel.

4.2.2 Experimental results

The pressurization operation charts obtained in these experiments are shown in **Fig. 4**. In Case 1, the temperature from the lower to upper regions inside the pressure vessel at 600 MPa ranged from 172 to 204℃ (temperature variation of 32℃), whereas in

Table 2 Specifications of WIP equipment with a high-pressure heat exchange

Maximum operating pressure	600MPa
Maximum operating temperature	200°C
Pressure medium	Hydraulic oil of high flash point
Diameter of working zone	120mm
Height of working zone	500mm
Thermocouple height (Thermocouple is inner work zone)	Upper / +450mm Middle / +300mm Lower / +150mm

Table 3 Experimental conditions of high-pressure heat exchange

	Case1	Case2
Operating pressure (MPa)	600	600
Temperature of pressure medium inner pressure vessel (before pressurizing) (°C)	160	160
Heating temperature of high-pressure piping by heat exchange system (°C)	60	200

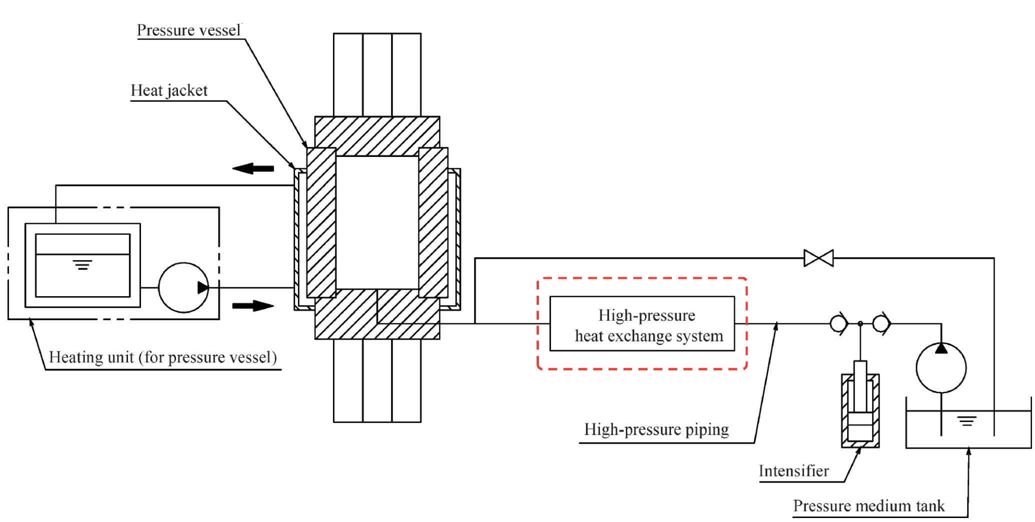

Fig. 3 System diagram of high-pressure heat exchange technology

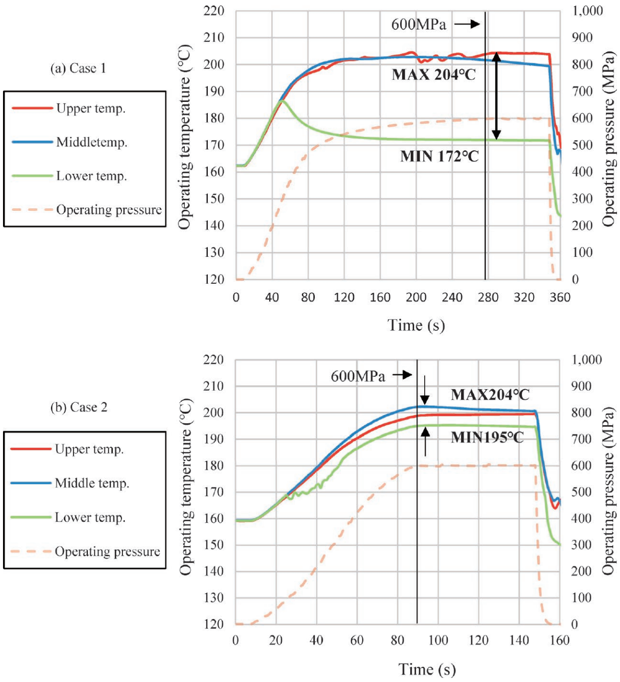

Fig. 4 Operation chart of high-pressure heat exchange for (a) Case 1 (heating temperature of high-pressure piping 60℃) and (b) Case 2 (heating temperature of high-pressure piping 200℃)

Case 2, the temperature from the lower to upper regions inside the pressure vessel ranged from 195 to 204℃ (temperature variation of 9℃), resulting in an improvement of 23℃ in temperature variation.

4.2.3 Discussion

In both cases 1 and 2, the temperatures at the upper and middle regions inside the pressure vessel remained within 195–205℃ when 600 MPa was reached. Meanwhile, in Case 1, a significant temperature drop was observed at the lower region inside the pressure vessel. These results suggested that the upper and middle regions inside the pressure vessel were not affected by the temperature of the pressure medium flowing in during pressurization and instead increase in temperature due to compression heat. By contrast, the lower region inside the pressure vessel were affected to a larger extent by the temperature of the pressure medium flowing in during pressurization.

Further improvements are necessary, such as by enhancing the heat exchange efficiency and forming a flow path for the pressure medium inside the pressure vessel to distribute the inflowing pressure medium to the upper part.

Conclusions

This paper described the development strategy and results of Kobe Steel's WIP equipment. Future studies should prototype large-scale WIP equipment, verify the effectiveness of high-pressure heat exchange technology, and connect this to commercialization and expansion while advancing the design of a uniform temperature structure inside the pressure vessel.

Production capacity must be improved by scaling up WIP equipment so that WIP equipment can be applied to the manufacturing process of all-solid-state batteries. We will steadily scale up WIP equipment, continue to support test processing, and conduct needs surveys for customers such as automobile and battery manufacturers to enable the adoption of WIP equipment in the manufacturing process of all-solid-state batteries.

References

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