Investigative Report by the Accident Investigation Committee for the Explosion & Fire Accident occurred in the High-Purity Polycrystalline Silicon Manufacturing Facility at Yokkaichi Plant of Mitsubishi Materials Corporation

(Abridged Version)

June 12, 2014

Accident Investigation Committee

1. Introduction

After the occurrence of an explosion and fire accident at Yokkaichi Plant of Mitsubishi Materials Corporation (MMC) on January 9, 2014, the Accident Investigation Committee was formed on January 17, 2014. The committee is composed of external academic experts and MMC's specialists with relevant knowledge and experience. A series of seven meetings were held from January 22 to June 6, 2014. This Investigative Report is a final report which clarifies direct causes leading to the accident and summarizes recommended preventive measures.

2. Overview of accident

Plant where accident occurred:	Yokkaichi Plant (No. 1 Plant) of Mitsubishi Materials Corporation
Equipment involved:	Water-cooled heat exchanger of No. 6 Hydrogen Recycling Facility
Date & time of accident:	January 9 (Thursday), 2014; 2:05pm Japan Standard Time
Casualty in personnel:	5 people were killed (3 employees of MMC, 2 employees of subcontractor companies) 13 people were injured (10 employees of MMC, 3 employees of subcontractor companies)
Damage to facilities:	Damage to surrounding facilities, etc.

3. Overview of plant and facilities where accident occurred

MMC's Yokkaichi Plant manufactures high-purity polycrystalline silicon used as raw materials in silicon wafers for semiconductors.

The water-cooled heat exchanger involved in the accident was installed in the hydrogen recycling facility shown in Fig.1.

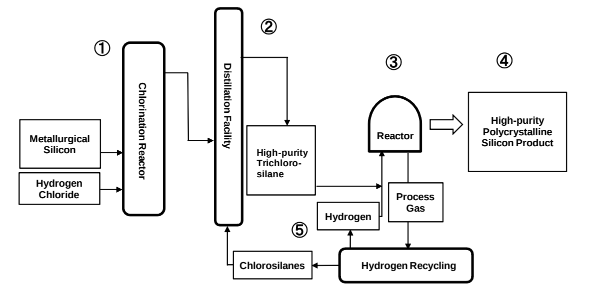

Fig. 1. Overview of high-purity polycrystalline silicon production process

As shown in Fig.2., multiple heat exchanger tubes were positioned inside the water-cooled heat exchanger. Process gases discharged from the reactor flowed through the heat exchanger tubes and were cooled by water flowing in the opposite direction on the outside.

4. Occurrence of accident

4.1. Events which led to explosion and fire accident

Nov. 27, 2013	The heat exchanger involved in the accident was removed from hydrogen recycling facility and placed in designated temporary storage place.
From Nov. 28, 2013	Dry nitrogen blow was performed for 3 days.
Dec. 3 to 27, 2013	Humidified nitrogen blow was performed for 20 days.
Jan. 6 to 8, 2014	Dry nitrogen blow was performed for 3 days.
Jan. 9, 2014	7:30am to 11:00am: The heat exchanger was transported to wash station. Dry nitrogen blow was performed. 11:00am to 1:00pm: Bottom channel cover was removed and cleaned. From 1:40pm: Procedures for opening top channel cover were started. 2:05pm: Top channel cover was opened. Explosion and fire occurred several seconds later.

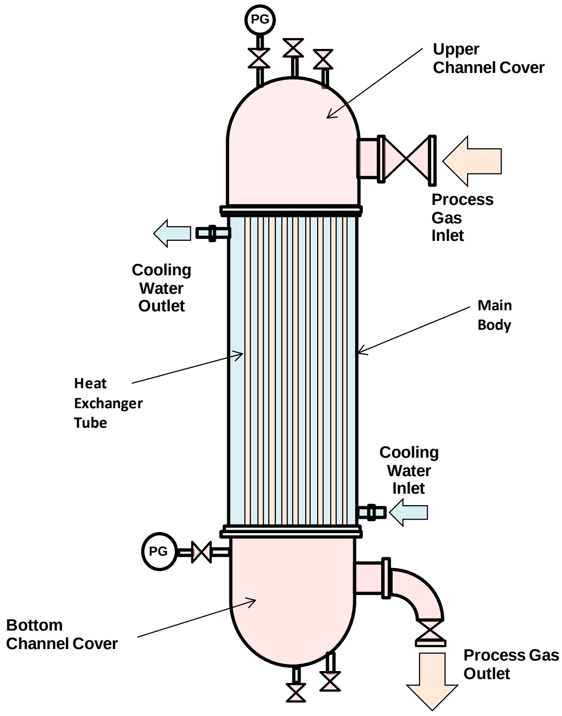

Fig. 2. Structural overview of heat exchanger (BH-HE-611)

4.2. Analysis for occurrence of explosion and fire accident

Based on interviews of external experts, evaluation by external specialized agencies and experiments by MMC, analysis was conducted for the following items.

(1) Investigation of explosion energy from analysis of explosion phenomena

The explosion energy was estimated from two separate phenomena at the accident site.

(2) Considerations on materials causing explosion and fire

The chemical structure and ignition and explosion properties were analyzed for the hydrolyzed products of chlorosilane polymers inside the heat exchanger. The estimated explosion energy was almost equivalent to the explosion energy from the above (1). Therefore, it is inferred that the hydrolyzed products of chlorosilane polymers were the materials caused the explosion. It is thought that the chlorosilane polymers scattered by the explosion and also decomposed to generate combustible materials which then erupted into the atmosphere and burned.

(3) Process of explosion and fire

The hydrolyzed products of chlorosilane polymers were ignited and exploded due to impact occurred at the flange surface where the upper channel cover was fastened to the body of the heat exchanger

→The top channel cover was sent flying.

→The blast shattered glass windows at the nearby building. Chlorosilane polymers remaining inside the heat exchanger were then sent flying.

→Combustible materials from chlorosilane polymers erupted into the atmosphere, burned and created a fireball.

5. FTA investigation for cause(s) of accident

5.1. Direct causes

The following items were identified as direct causes of the explosion and fire accident at the heat exchanger.

(1) Low-temperature hydrolysis of chlorosilane polymers generated materials with high ignition and explosion sensitivity, and large explosion energy.

(2) Dry conditions induced an increase in the ignition and explosion sensitivity and the explosion energy of the hydrolyzed products of chlorosilane polymers. The ignition and explosion was caused by an unidentified impact which acted as an ignition source when the top channel cover of the water-cooled heat exchanger was opened.

(3) Lack of sufficient and accurate public scientific information regarding the risks of ignition and explosion for the hydrolyzed products of chlorosilane polymers, their generation process, and appropriate humidified processing conditions for chlorosilane polymers, led to insufficient consideration of the appropriate safety measures.

Furthermore, direct causes of casualty in personnel were the top channel cover being blown by the ignition and explosion, the blast, and the ensuing fire. The presence of nearby workers resulted in a greater amount of personal injury.

5.2. Indirect causes

The following items were identified from FTA(*) as causes other than direct causes, i.e. indirect causes.

(*)FTA (Fault Tree Analysis): A method of deductive failure analysis in which a tree diagram is used to resolve an undesired event into its causes.

(1) Risk assessment

Due to a lack of knowledge regarding the ignition and explosive properties of the hydrolyzed products of chlorosilane polymers which was a direct cause of the accident, as a management issue, there were insufficient risk assessments for handling of chlorosilane polymers.

(2) Safety management for heat exchanger

It was confirmed that the process gas flow through the heat exchanger involved in the accident was not blocked by an accumulation of chlorosilane polymers. Therefore, while no correlation was found between the accident and safety management for the heat exchanger, it is recommended to establish the management methods of the heat exchanger.

(3) Standard Operating Procedures

As the result of insufficient knowledge regarding the ignition and explosion properties of the materials which were a direct cause of the accident, their risks were not reflected sufficiently into standard operating procedures. Also, some contents of those procedures lacked objectiveness and specificity, and relied on workers' experiences.

(4) Training, etc.

As the result of insufficient knowledge regarding their properties, the risks were not reflected sufficiently into training. Also, there existed insufficient confirmation methods to properly evaluate the workers for the training efficiency and their compliance to the rules.

6. Recommendations for preventive measures

The Committee provided recommendations for preventive measures and reviewed the validity of practices and policies by MMC in response to those preventive measures.

6.1. Consideration of preventive measures against ignition and explosion during maintenance of heat exchangers

(1) Methods for opening and cleaning heat exchangers

1. The amount of chlorosilane polymers is measured. The hydrolysis process time and amount of generated gas is calculated. During transportation to the maintenance area, a safe condition should be created using inert gas enclosure. At the maintenance area, required pipes, etc. are connected.
2. Hydrolysis should be conducted while keeping the inside of the heat exchanger full of water. After filling the exchanger with water, a water temperature of approximately 40 degrees Celsius is maintained during hydrolysis. Appropriate data are measured and monitored. The ending point for hydrolysis is determined from pH and hydrogen concentration.
3. The channel cover is opened by remote control.
4. High-pressure water is used to wash away chlorosilane polymers and the hydrolysis products of chlorosilane polymers from inside the heat exchanger. Wastewater is discharged into a sump pit under moist conditions.
5. In the sump pit of the existing wastewater treatment facilities is used to neutralize the top clear layer of discharged water and dispose of externally. Residue is then crushed, ground, neutralized and disposed of as industrial waste under the safe conditions.

(2) Facilities for opening/washing the heat exchanger

In order to ensure safety on opening and washing the heat exchanger, it is necessary to install new dedicated facilities with the following functions.

・Installation of protective walls against the explosion.

・Enable opening of the channel cover using remote control.

・Enable safe processing of exhaust gas.

・Enable temperature control and monitoring of hydrolysis.

6.2. Strengthening of safety management

The Committee recommended strengthening of safety management as a measure for decreasing risk and improving safety at the plant.

(1) Reduction of risk via hazard extraction and risk assessment

1. FTA is used to create a hazard checklist and implement countermeasures.
   For all hazards identified through FTA, a checklist is created which shows specific countermeasures to be implemented, implementation schedule and progress status. It is confirmed that appropriate measures are formulated.
2. Risk assessment is conducted for materials, facilities and operations
   Risk assessment is conducted if new knowledge is obtained regarding materials or if there is a change in facilities. It is reflected as necessary to ensure safe operations. Also, it is important to cooperate with subcontractor companies on conducting risk assessment.
3. Residual risk associated with handling of similar hazardous materials is decreased.
   Case histories and near-misses are analyzed. Processes are extracted for the handling of chlorosilane polymers. Risk assessment is conducted again based on new knowledge gained during this accident investigation. It is necessary to continually implement measures to decrease risk in the future. Also, it was confirmed that in the manufacturing line there were no processes with the same handling conditions of the materials which was a direct cause of the accident.

(2) Systemization of safety and health manuals, reformation of standard operating procedures

1. Required contents for standard operating procedures
   In order to improve the standard operating procedures with vague judgment criteria and operators' experience, it is necessary to establish new rules which define the required contents and caution points etc. for standard operating procedures.
2. Classification of standard operating procedures according to degree of danger (size of effect) and revision of risk assessment procedures
   For operations with a high degree of danger (size of effect), it is important to perform risk assessment again even if those operations were judged as having a low priority in risk response. and to reconfirm safety from the perspectives of current facilities, operation and management. Specifically, it is necessary to classify standard operating procedures according to the degree of danger (size of effect), and based on that classification, to assign priority to staff with inspection and approval authority .
3. Comprehensive inspection of standard operating procedures

Starting from items with a high degree of danger (size of effect), it is important to perform sequential and comprehensive inspection of standard operating procedures, to conduct training for employees and to ensure thorough compliance. Also, it is necessary to receive validation from a third party when revising operation standards and to revise again as necessary.

4. Assigned duties of safety administrators

   It is necessary to clarify the duties, the date of election and dismissal, and the responsibilities of safety administrators in relation to hazardous operations.

5. Follow-up for near-misses

   It is important to promote increased reporting activities for near-misses. Also, in addition to reporting near-miss cases to the Safety and Health Committee, follow-up should be conducted for the status of countermeasure implementations.

6. Follow-up system for corrective actions

   In the future, it is necessary to conduct systematic follow-up for the status of corrective actions etc. in relation to major accidents and disasters.

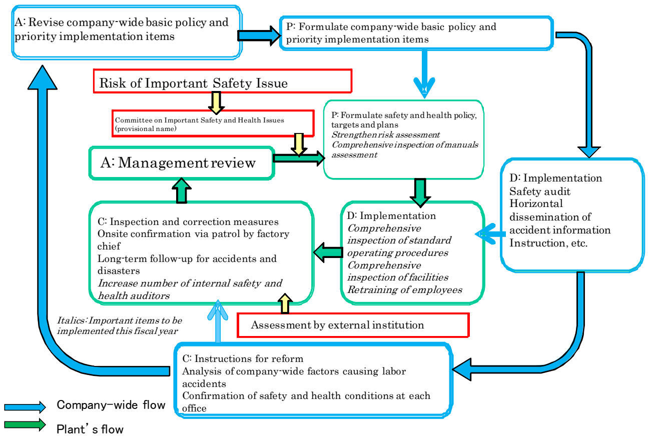

Fig. 3. Continuous improvements through Safety and Health Management System

(3) Retraining

In order to raise awareness for safety management measures and to ensure reliable implementation of safe operation, it is necessary to conduct periodic safety training for MMC employees and employees of subcontractor companies.

(4) Utilize PDCA cycle to continuously strengthen safety management

As shown in Fig. 3., it is important to construct a safety and health management system with active involvement from MMC headquarters and to conduct continual improvement by executing the PDCA cycle.

[Strengthening safety management of MMC]

Regarding safety activities of MMC, in addition to the contents of company-wide labor safety and health activities, the Committee confirmed the following responses by headquarters following the accident: implementation of emergency safety patrols, inspection of hazardous procedures and standard operating procedures, establishment of a Safety Declaration Day (January 9), strengthening of organizations related to safety and health, starting a New Zero-Accident Project, and strengthening of safety auditing.

<u>6.3. Review of background factors and fostering of safety culture</u>

The Committee reviewed background factors such as environmental and organizational factors with the potential to influence safety and recommended a direction for improvement measures.

Furthermore, the Committee affirmed MMC's policies in response to those measures.

(1) Review of background factors

As the result of investigative hearings of plant personnel by an external organization, the following background factors were identified.

Background factors related to safety infrastructure

- Insufficient systematic training.
- Insufficient transfer of technology.

Background factors related to safety culture

- Low sensitivity to danger.
- Insulation from outside information/events (like a "frog at the bottom of a well").

(2) Countermeasures for background factors

Based on results of the review, the Committee believes that it is essential to formulate reform measures over the long-term.

1. Development of systematic training method and curriculum
   - Development of a method and curriculum for systematic training on chemical knowledge, processes and operation standards etc.
   - Systematic cultivation of personnel through training based on accident case histories, transfer of experience from skilled workers, and measures to strengthen emergency response ability etc.
2. Strengthening the safety infrastructure through establishment of a dedicated process technology department, cooperation between headquarters and the plant, and cooperation with external institutions, etc.
3. Strengthening safety management functions through revision of plant organizations.
4. Establishment of a system for continual reform

   It is important to construct a system for incorporating external assessments and information. and to implement continuous reforms to foster safety culture.

(3) System to implement measures for background factors

It is necessary to organize a "Yokkaichi Plant Safety Culture Rebuilding Project" with a leading role played by the Safety and Health Division of MMC headquarters and to use a PDCA cycle to incorporate assessment by external organizations etc. and apply to continuous reform.