In situ Observation of Formation of Fe-Zn Intermetallic Compounds During Galvannealing Process by X-ray Diffraction

Galvannealed steel sheets are widely used in the automotive industry to protect car bodies from corrosion. In the industrial process of galvannealed steel sheets, steel substrates are dipped in molten zinc containing a small amount of aluminum, then annealed in a furnace at about 500 ℃. Since the coating of the galvannealed steel sheets mainly consists of Fe-Zn intermetallic compounds, such as $FeZn_7$ (δ_1 phase) and $FeZn_{13}$ (ζ phase), it is very important to study the growth behavior of those compounds during a galvannealing process to understand the roughness or the mechanical properties of the coating after the process.

As summarized by Horstmann [1], many reports on hot-dip galvanizing reactions have been presented. However, because those reactions occur in a short period up to 60 seconds, it is very difficult to detect them with static analyses using the specimen quenched after annealing, such as a cross-sectional observation of the coating with an electron microscope or the measurement of the iron content of the coating. Therefore, a rapid detection system is required to observe those reactions dynamically, *i.e.*, "*in situ* observation." In order to perform the "*in situ* observation," penetration depth of the X-ray and time definition of the detector are important factors because it is necessary to observe the whole coating with a 10 ~ 20 µm thickness, and to observe the reaction finishing within 60 seconds. An easy way to achieve good time definition of the detector is to increase the source intensity. Therefore, the X-ray source, being able to penetrate deeply, *i.e.*, having high energy and high intensity, is necessary for the "*in situ* observation."

In this study, synchrotron radiation was used as

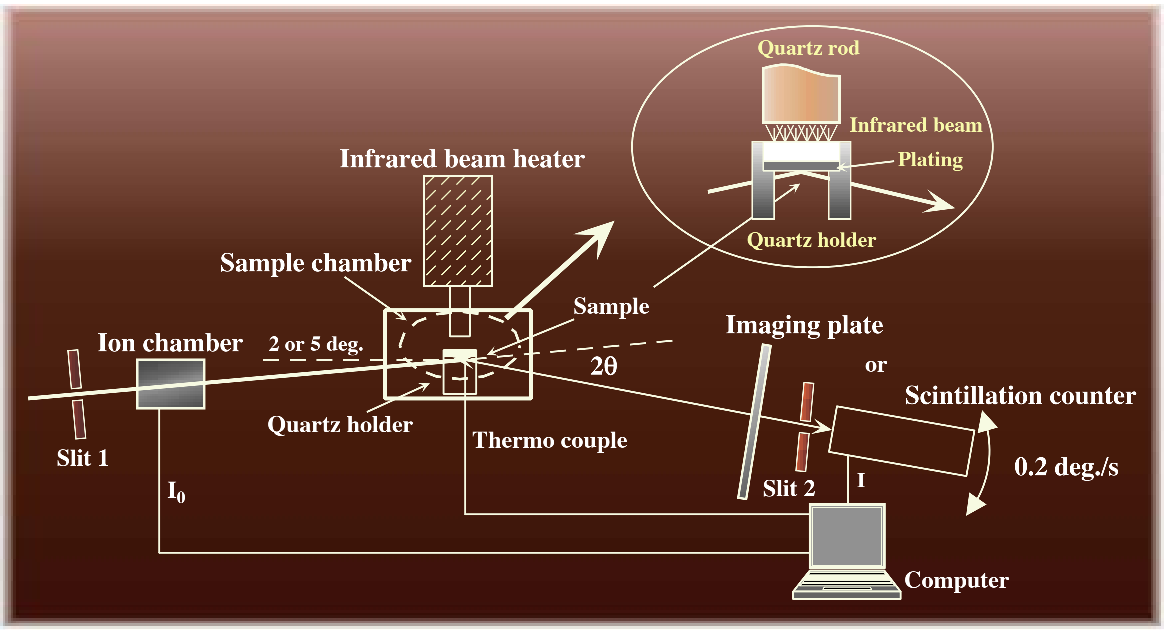

Fig. 1. Schematic illustration of the in situ observation system.

the X-ray source and the experiments were performed at beamline **BL19B2** [2]. The schematic illustration of the *in situ* observation system is shown in Fig. 1. The galvanized steel sheet sample was mounted on a quartz holder in the sample chamber filled with N_2 gas, and was heated from the polished side with the infrared beam heater (Thermo Riko: GA152) mounted on the 8-axis goniometer. We obtained heating time-dependent diffraction peak profiles with either a scintillation counter or an imaging plate. When the scintillation counter was used, the peak profiles were measured at intervals of 5 seconds while being scanned at an angle velocity of 0.2 degrees per second. When the imaging plate was used, the peak profiles were measured every second.

Figures 2(a) and 2(b) show diffraction peak profiles obtained with a scintillation counter and an imaging plate, respectively. The samples had zinc coatings containing small amounts of aluminum. Heating time shown in the figures was started to be counted when the coating fully melted. An increase in the diffraction peak intensity identified as δ_1(330) was successfully observed in the profiles. The diffraction peak could not be observed in profiles up to 20 seconds after the coating melted in Fig. 2(a), therefore, it is considered that the 30-μm coating, was too thick to allow detection of the diffraction peaks of the δ_1 phase growing near the interface between the coating and the steel substrate at the beginning of the annealing process.

On the other hand, the diffraction peak could not be observed up to 7 seconds after the coating melted in Fig. 2(b). In this measurement, the thickness of the coating does not affect the observation of the diffraction peaks of the δ_1 phase growing near the interface as mentioned above, because the steel substrate's diffraction peak was obtained clearly. It is well known that aluminum in the coating forms an Al-rich layer between the

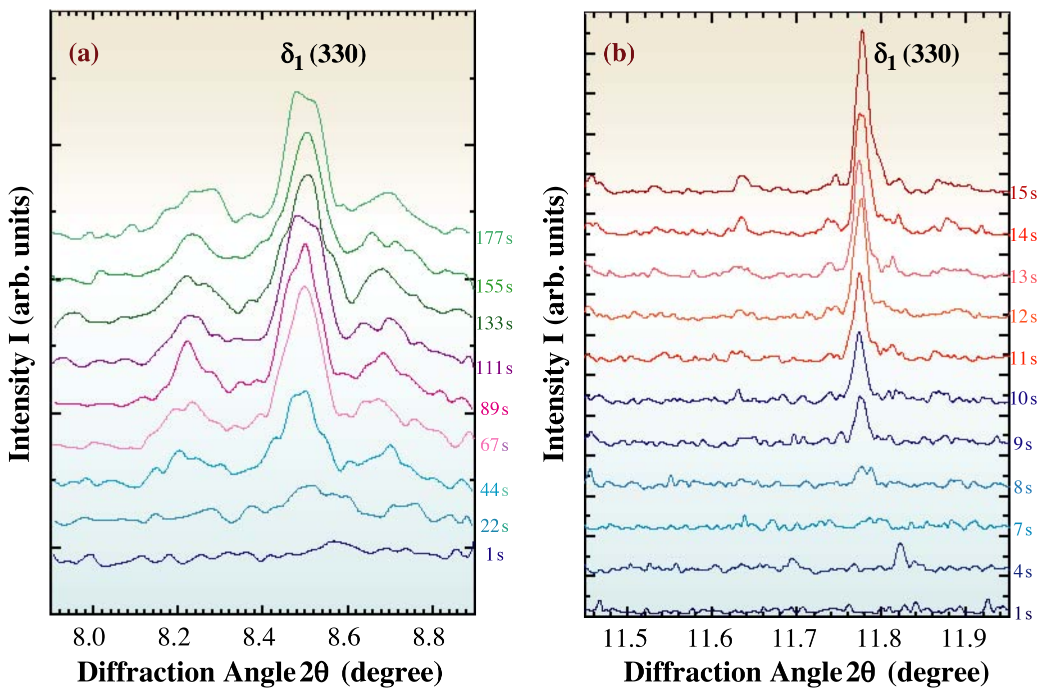

*Fig. 2. Diffraction profiles obtained from galvanized steel sheet during annealing. **(a)** Wavelength of incident X-ray: 0.0319 nm; thickness of the coating: 30 μm; detector: scintillation counter. **(b)** Wavelength of incident X-ray: 0.0443 nm; thickness of the coating: 10 μm; detector: imaging plate.*

coating and the steel substrate, retarding the growth of Fe-Zn intermetallic compounds [3]. Therefore, the variation of peak profiles indicates that the Al-rich layer prevents the growth of δ_1 phase at the beginning of the annealing process. The period from the beginning of annealing to the beginning of Fe-Zn intermetallic compound growth is called an "incubation period."

Assuming that the δ_1 phase grows in a layer-by-layer manner, the time dependence of thickness was estimated as shown in Fig. 3. The estimated thickness of the δ_1 phase increased by the parabolic law with annealing time, taking into account the incubation period (t_{inc}). These results suggest that the growth of δ_1 phase is dominated by a diffusion of Fe atoms and Zn atoms in the coating.

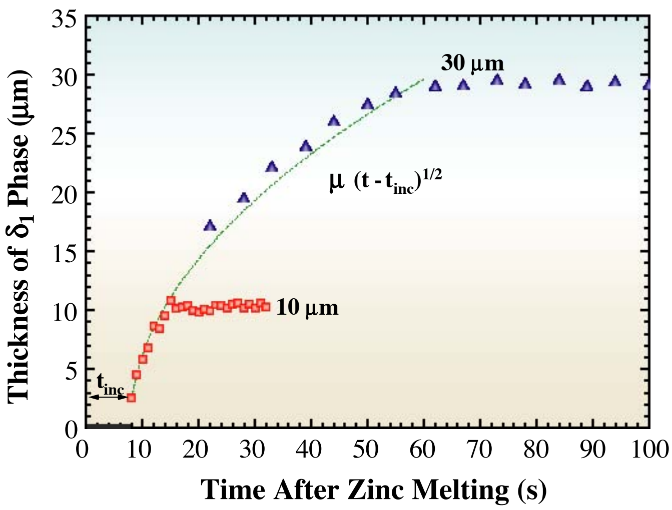

Fig. 3. Relationship between estimated thickness of the δ_1 phase and annealing time.

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